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Phosphoranes. 4. Methylbis(trifluoromethyl)phosphoranes, $CH_3(CF_3)_2PXY$, with Monofunctional [F, Cl, OCH_3, $N(CH_3)_2$] Substituents

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Direct oxidation of $CH_3(CF_3)_2P$ with Cl_2 yields the new phosphorane $CH_3(CF_3)_2PCl_2$ from which $CH_3(CF_3)_2PF_2$, $CH_3(CF_3)_2P(F)OCH_3$, $CH_3(CF_3)_2P(OCH_3)_2$, and $CH_3(CF_3)_2P(F)N(CH_3)_2$ can be obtained by appropriate metathetical substitution reactions. Alternate synthesis of $CH_3(CF_3)_2PF_2$ can be achieved by methylation of $(CF_3)_2PF_3$ with $(CH_3)_4Sn$. Variable-temperature ^{19}F NMR spectroscopy of $CH_3(CF_3)_2PX_2$ (X = F, Cl) is consistent with axial location of the halogens on the trigonal-bipyramidal framework in both cases. The substituted monofluorides $CH_3(CF_3)_2P(F)Y$ ($Y = OCH_3$, $N(CH_3)_2$) show two nonequivalent (axial and equatorial) CF_3 environments in the low-temperature ^{19}F NMR spectrum. At very low temperatures the axial CF_3 signals in $CH_3(CF_3)_2P(OCH_3)_2$ split into a clear AB_2 pattern due to stopped rotation of OCH_3 and/or CF_3 groups. Heating $CH_3(CF_3)_2P(F)N(CH_3)_2$ yields principally $CH_3(CF_3)PF_2N(CH_3)_2$ presumably by means of CF_2 elimination. Other thermolysis products (e.g., CF_3H) are also found which suggest the participation of other processes. Decomposition of the postulated intermediate $CH_3(CF_3)_2P(Cl)OCH_3$ during synthesis of $CH_3(CF_3)_2P(OCH_3)_2$ from $CH_3(CF_3)_2PCl_2$ is thought to be responsible for the formation of $CH_3(CF_3)_2PO$ in the reaction.

Introduction

Recent studies of the chemistry and stereochemistry of phosphoranes containing CF_3 groups[1,2] indicated that the position of the CF_3 substituents in the five-coordinate framework can be deduced from the NMR spectral parameters.[3] We describe herein a series of trialkylphosphoranes containing two CF_3 groups, one methyl group, and a variety of monofunctional substituents [F, Cl, OCH_3, $N(CH_3)_2$] which provide additional evidence in support of this proposal. In addition low-temperature NMR spectroscopic studies reveal further details of the intramolecular rearrangement processes which occur in these molecules.

Results and Discussion

A. Synthetic Considerations. Chlorine smoothly oxidized methylbis(trifluoromethyl)phosphine to the dichlorophosphorane $CH_3(CF_3)_2PCl_2$ in good yield in a manner analogous to the behavior of $(CF_3)_3P$[4]

$$CH_3(CF_3)_2P + Cl_2 \rightarrow CH_3(CF_3)_2PCl_2 \qquad (1)$$

The fluorophosphorane was obtained by fluorination of the chlorophosphorane with antimony trifluoride

$$CH_3(CF_3)_2PCl_2 \xrightarrow{SbF_3} CH_3(CF_3)_2PF_2 \qquad (2)$$

or by methylation of $(CF_3)_2PF_3$ with $(CH_3)_4Sn$[5]

$$(CF_3)_2PF_2 + (CH_3)_4Sn \rightarrow CH_3(CF_3)_2PF_2 + (CH_3)_3SnF \qquad (3)$$

Although good yields were obtained in both cases, the latter route is potentially less useful because some of the reactant is lost to salt formation[6]

$$(CF_3)_2PF_3 + (CH_3)_3SnF \rightarrow [(CH_3)_3Sn][(CF_3)_2PF_4] \qquad (4)$$

but only a small quantity of the complex salt was found in the solid residues. $(CH_3)_4Sn$ is difficult to separate from $CH_3(CF_3)_2PF_2$;[5] however, the use of excess $(CF_3)_2PF_3$ followed by careful fractionation leads to relatively pure product.

Simple substitution of both of the halogenophosphoranes was effected by means of the silane reagents[7] $(CH_3)_3SiY$; for example, reaction of $CH_3(CF_3)_2PCl_2$ with excess methoxytrimethylsilane gave methylbis(trifluoromethyl)dimethoxyphosphorane, $CH_3(CF_3)_2P(OCH_3)_2$, in variable yield along with $CH_3(CF_3)_2PO$[8]

$$\begin{aligned} &CH_3(CF_3)_2PCl_2 + 2(CH_3)_3SiOCH_3 \rightarrow (1-x)CH_3(CF_3)_2P(OCH_3)_2 \\ &\quad + xCH_3(CF_3)_2PO + (2-x)(CH_3)_3SiCl + xCH_3Cl \qquad (5) \end{aligned}$$

Interestingly, the best yield of the dimethoxyphosphorane was obtained if the reaction was carried out in the presence of a catalytic amount of iodine. In the absence of iodine $CH_3(CF_3)_2PO$ constituted about 50% of the phosphorus-containing products. The formation of equal proportions of $CH_3(CF_3)_2PO$ and CH_3Cl in reaction 5 suggested that the partially substituted chlorophosphorane $CH_3(CF_3)_2P(OCH_3)Cl$ was unstable and decomposed to the phosphine oxide and methyl chloride

$$CH_3(CF_3)_2P(OCH_3)Cl \rightarrow CH_3(CF_3)_2PO + CH_3Cl \qquad (6)$$

The dimethoxyphosphorane $CH_3(CF_3)_2P(OCH_3)_2$ is stable under normal conditions and is easily handled under vacuum. The phosphine oxide was alternatively prepared by reaction of the phosphine $CH_3(CF_3)_2P$ with NO_2,[9] an easier method than those used initially to prepare this compound.[8]

The partially substituted fluorophosphoranes $CH_3(CF_3)_2P(F)Y$ [$Y = OCH_3$, $N(CH_3)_2$] were synthesized from $CH_3(CF_3)_2PF_2$ and equimolar quantities of the appropriate trimethylsilane derivative $(CH_3)_3SiY$

$$\begin{gathered} CH_3(CF_3)_2PF_2 + (CH_3)_3SiY \rightarrow CH_3(CF_3)_2P(Y)F + (CH_3)_3SiF \qquad (7) \\ Y = OCH_3,\ N(CH_3)_2 \end{gathered}$$

The mono(dimethylamino) derivative was also obtained by direct gaseous aminolysis of the fluorophosphorane with dimethylamine

$$\begin{aligned} &2CH_3(CF_3)_2PF_2 + 3(CH_3)_2NH \rightarrow 2CH_3(CF_3)_2P[N(CH_3)_2]F \\ &\quad + (CH_3)_2NH_2HF_2 \qquad (8) \end{aligned}$$

A large excess of dimethylamine under more strenuous conditions did not effect further substitution of the remaining fluorine substituent. Further heating led to the thermal decomposition of the monofluorophosphorane by CF_2 elimination and other processes.

Table I. Hydrolysis of Phosphoranes $CH_3(CF_3)_2PXY$

Compd	pH	Quantity, g (mmol)	CF_3H evolved, g (mmol)	Ion in soln
$CH_3(CF_3)_2$-PCl_2	Neut	0.182 (0.71)	0.049 (0.70)	$CH_3(CF_3)PO_2^-$
	Alk	0.188 (0.74)	0.105 (1.49)	$CH_3PO_3^{2-}$
$CH_3(CF_3)_2$-PF_2	Neut	0.076 (0.34)	0.023 (0.33)	$CH_3(CF_3PO_2^-$
	Alk	0.113 (0.51)	0.070 (1.00)	$CH_3PO_3^{2-}$
$CH_3(CF_3)_2$-$P(OCH_3)_2$	Neut	0.115 (0.47)	0.032 (0.46)	$CH_3(CF_3)PO_2^-$
	Alk	0.878 (0.76)	0.106 (1.51)	*a*
$CH_3(CF_3)_2$-$P(F)OCH_3$	Neut	0.171 (0.73)	0.049 (0.70)	$CH_3(CF_3)PO_2^-$
	Alk	0.124 (0.53)	0.072 (1.03)	$CH_3PO_3^{2-}$
$CH_3(CF_3)_2P$-$(F)N(CH_3)_2$	Neut	0.108 (0.44)	0.030 (0.44)	$CH_3(CF_3)PO_2^-$
	Alk	0.109 (0.44)	0.062 (0.88)	$CH_3PO_3^{2-}$

[a] Not investigated.

Attempts to prepare $CH_3(CF_3)_2P(SCH_3)F$ from the fluorophosphorane and (methylthio)trimethylsilane, $(CH_3)_3SiSCH_3$, were unsuccessful. No change was observed according to the NMR spectrum after 7 days in contact at room temperature.

Neutral hydrolysis (Table I) of the phosphoranes yielded 1 molar equiv[10] of CF_3H with the $CH_3(CF_3)PO_2^-$ ion[11] remaining in solution

$$CH_3(CF_3)_2PXY + 2H_2O \rightarrow CF_3H + CH_3(CF_3)PO_2^- + HX + HY + H^+ \qquad (9)$$

$$X = Y = F, Cl, OCH_3; X = F, Y = OCH_3, N(CH_3)_2$$

Alkaline hydrolysis (Table I) gave 2 molar equiv[10] of CF_3H leaving the $CH_3PO_3^{2-}$ ion[12] in solution

$$(CF_3)_2P(CH_3)XY + 3H_2O \xrightarrow{OH^-} 2CF_3H + CH_3PO_3^{2-} + HX + HY + 2H^+ \qquad (10)$$

$$X = Y = F, Cl, OCH_3; X = F, Y = OCH_3, N(CH_3)_2$$

The infrared spectral data are summarized in Table II and the data for $CH_3(CF_3)_2PF_2$ are in good agreement with those of Sawin.[5] Bands associated with C–H stretching frequencies and with P–CF_3 and P–CH_3 structural units[8b,13,14] are observed in the expected regions. The spectra of $CH_3(CF_3)_2P(OCH_3)_2$ and $CH_3(CF_3)_2P(OCH_3)F$ show strong bands at about 1070 and 760 cm^{-1}, which can be assigned as ν_{P-O-C} and ν_{P-O}, respectively. The band at 795 (790[5]) cm^{-1} in the spectrum of $CH_3(CF_3)_2PF_2$, at 820 cm^{-1} in the spectrum of $CH_3(CF_3)_2P(OCH_3)F$, and at 780 cm^{-1} in the spectrum of $CH_3(CF_3)_2P[N(CH_3)_2]F$ can be assigned to P–F stretching vibrations,[13] and the strong band at 1010 cm^{-1} is undoubtedly due to PNC_2 structural feature in the molecule.

In common with other fluoro-[15] and trifluoromethylphosphoranes[1,2] the mass spectra of $CH_3(CF_3)_2PXY$ show no parent ions, but the characteristic fragments, confirmed by mass measurement (Table III), correspond to the formation of $CH_3(CF_3)_2P^{35}Cl^+$ and $CH_3(CF_3)_2P^+$ from $CH_3(CF_3)_2PCl_2$; $CH_3(CF_3)_2PF^+$ from $CH_3(CF_3)_2PF_2$; $CH_3(CF_3)_2POCH_3^+$, $CH_3(CF_3)PF(OCH_3)^+$, and $CH_3PF_2(OCH_3)^+$ from $CH_3(CF_3)_2P(OCH_3)_2$; $CH_3(CF_3)_2P(OCH_3)^+$ and $CH_3(CF_3)_2PF^+$ from $CH_3(CF_3)_2P(OCH_3)F$; and $CH_3(CF_3)_2P[N(CH_3)_2]^+$ and $CH_3(CF_3)_2PF^+$ from $CH_3(CF_3)_2P[N(CH_3)_2]F$. These data strongly suggest that these ions are derived from the indicated parent molecules by loss of one of the X

Table II. Infrared Spectral Data for $CH_3(CF_3)_2PXY$[a,b]

X = Cl Y = Cl	X = F Y = F	X = OCH_3 Y = OCH_3	X = F Y = OCH_3	X = F Y = $N(CH_3)_2$	
		3025 w	3025 w		ν(CH)
		2970 m	2980 m	2960 m	
2940 vw	2940 vw		2920 vw	2920 sh	
	2920 vw				
		2860 w	2870 w	2890 m	
				2830 w	
				2780 w	
	2420 w				
2260 w	2280 w				Overtone
	1405 w	1470 w	1460 w	1465 m	$\delta_{asym}((P)CH)$
	1315 m	1310 w	1315 w	1310 w	$\delta_{sym}((P)CH)$
				1285 m	
		1205 vs			
1210 m, sh					
1180 vs	1218 vs	1205 vs	1225 vs	1205 vs	ν(CF)
	1200 sh	1185 m	1190 vs	1170 vs	
1145 vs	1160 s		1160 vs	1140 vs	
1115 m, sh	1145 sh	1130 vs	1115 vs	1115 m	
				1085 s	
		1070 m	1075 s		ν((P)O–C)
				1010 s	$\nu((P)NC_2)$
955 m	970 m	960 m	970 m	965 w	$\gamma(PCH_3)$
865 m	890 s	880 m	885 m	885 m	
		850 w		795 w	
	795 vs		820 m	780 m	ν(PF)
		785 m	740 m		ν(P–O)
740 m	735 m	750 w		745 w	$\delta_{sym}(CF_3)$
			700 m	725 w	
			670 vs	665 s	
				645 s	
560 m	570 s	580 s	565 w	565 m	$\delta_{asym}(CF_3)$
			545 w		
525 m	530 m	525 m	530 w	500 w	
500 m					ν(PCl)
	460 s				
		490 w	470 m	455 w	
415 w		430 w	430 w		

[a] Gas-phase spectra; all values in cm^{-1}. Abbreviations and symbols: s, strong; m, medium; w, weak; v, very; sh, shoulder; ν, stretch; δ, deformation; γ, rock; sym, symmetric; asym, asymmetric. [b] Values for $CH_3(CF_3)_2PF_2$ are in agreement with those of Sawin.[5]

Table III. Mass Measurement Data for $CH_3(CF_3)_2PXY$ Fragments

Compd	Ion[a]	Mass	
		Calcd	Found
$CH_3(CF_3)_2PF_2$	$CH_3(CF_3)_2PF$	202.9860	202.9854
$CH_3(CF_3)_2PCl_2$	$CH_3(CF_3)_2P^{35}Cl$	218.9565	218.9572
	$CH_3(CF_3)_2P$	183.9876	183.9878
$CH_3(CF_3)_2P(OCH_3)_2$	$CH_3(CF_3)_2POCH_3$	215.0059	215.0057
	$CH_3(CF_3)PF(OCH_3)$	165.0094	165.0100
	$CH_3PF_2(OCH_3)$	115.0124	115.0123
	$P(OCH_3)_2$	93.0106	93.0107
$CH_3(CF_3)_2PF(OCH_3)$	$CH_3(CF_3)_2POCH_3$	215.0059	215.0057
	$CH_3(CF_3)_2PF$	202.9860	202.9854
$CH_3(CF_3)_2PF[N(CH_3)_2]$	$CH_3(CF_3)_2PN(CH_3)_2$	228.0376	228.0384
	$CH_3(CF_3)_2PF$	202.9860	202.9910

[a] Reasonable structural formulas are given for ease of identification only.

or Y substituents or elimination of CF_2.[16] The mass spectral data are given in Table IV. Notably the mass spectrum of $CH_3(CF_3)_2PF_2$ is dominated by the ions $CH_3PF_3^+$ (*m/e* 103, 22.8%) and $CH_3(CF_3)PF_2^+$ (*m/e* 153, 20.7%) in addition to the strong component due to CF_3^+ or PF_2^+ (*m/e* 69, 23.1%). The mass spectrum of $CH_3(CF_3)_2P(F)OCH_3$ is dominated by ions at *m/e* 165 (23.2%, $CH_3(CF_3)PF(OCH_3)^+$) and 115 (17.9%, $CH_3PF_2(OCH_3)^+$) and the spectrum of $CH_3(CF_3)_2P(OCH_3)_2$ is dominated by $CH_3(CF_3)P(OCH_3)_2^+$ (*m/e* 177, 17.33%).

Pyrolysis of $CH_3(CF_3)_2P(F)N(CH_3)_2$ at 70 °C yielded $CH_3(CF_3)PF_2N(CH_3)_2$, identified by comparison of properties with an authentic sample prepared and characterized separately,[17] in about 25% yield as the expected result of thermal CF_2 elimination.[2a,18] It is notable that the cyclic perfluoropropane or -butane normally encountered[2a,18] was not observed probably as a result of competitive addition reactions which occur under the conditions employed. In addition to the isolated difluoride the only volatile product was a 67% yield of CF_3H. A mixture of involatile fluorine–phosphorus compounds remained in the reaction vessel and was not characterized. The occurrence of CF_3H suggests that the pyrolysis does not proceed with only CF_2 elimination, but there are not sufficient data available to identify these other processes at this time.

NMR Spectra and Stereochemistry of Phosphoranes. If we assume, as before,[1-3] that these monofunctionally substituted phosphoranes possess trigonal-bipyramidal molecular structures analogous to those of the methylfluorophosphoranes[19] and if we further consider only those isomers in which CH_3 resides in the equatorial plane,[19,20] then only three trigonal-bipyramidal ground-state structures are possible (Figure 1) depending on the relative preferences of the substituents X and Y for axial or equatorial location.

Analysis of the ^{19}F NMR spectral patterns arising from the trifluoromethyl groups employing the magnitude of $^2J_{PF}$ as the indicator of the location of the CF_3 group on the trigonal-bipyramid framework[1-3] leads to a consistent assignment of the ground state of each of the present series of molecules. While a few cases remain somewhat ambiguous, it is important to note that alternative interpretations of the data provide consistently inferior structural predictions and in no case does any of the NMR evidence contradict the basic assumption of the trigonal-bipyramidal structural framework or the assumption that CH_3 is consistently located in the equatorial plane in the ground-state structures of these molecules. The NMR data are summarized in Table V.

The NMR spectral behavior of the two dihalogenophosphoranes $CH_3(CF_3)_2PX_2$ (X = F, Cl) strongly indicates that the appropriate ground-state structure in both cases is A (Figure 1), even though the electronegativity rule[20] would predict structure C (X = Y = Cl) with diequatorial Cl substituents.

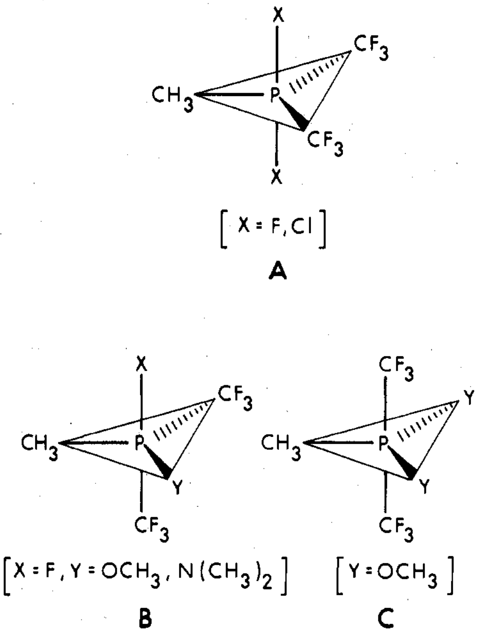

Figure 1. Ground-state structures of $CH_3(CF_3)_2PXY$ phosphoranes.

The normal (+33 °C) temperature ^{19}F NMR spectra of the CF_3 region of both compounds consisted of a simple doublet (X = Cl) and a doublet of triplets (X = F), expected from the coupling of P and, in the latter case, two equivalent fluorine atoms with the CF_3 groups. No discernible proton–fluorine coupling was observed probably because of its low magnitude. The directly bound P–F region consisted of a major doublet each component of which was split due to $^3J_{FF}$ coupling. The ^1H and ^{19}F NMR spectra of methylbis(trifluoromethyl)difluorophosphorane therefore strongly support the formulation of the compound as a phosphorane rather than an isomeric phosphonium salt.

No significant change was observed in the CF_3 portion of the ^{19}F NMR spectrum of either compound upon cooling the samples to −100 °C suggesting that either any positional averaging process is fast and prevents the detection of different CF_3 environments or, and in our opinion more likely, the ground-state structure of the molecule is A at all temperatures. While the data at hand cannot unambiguously prove the latter postulate, comparison of the magnitude of $^2J_{PF}$ (154 and 134 Hz, respectively) with the numerical values obtained on systems in which CF_3 groups appear to be clearly located in the equatorial plane (vide infra and elsewhere[1-3]) strongly support the assignment of the ground-state structure A to these compounds. These magnitudes are also comparable to the corresponding values of $^2J_{PF}$ exhibited[2,3,20,21] by $(CF_3)_3PF_2$, $(CF_3)_2PF_3$, and CF_3PF_4 which also appear[24] to possess ground-state structures in which CF_3 groups consistently occupy equatorial locations. Available vibrational analyses support this conclusion.[22]

The normal (+33 °C) temperature ^1H NMR spectra of both compounds consist of a complex doublet (X = Cl, $^2J_{PH}$) or a complex doublet of triplets (X = F, $^2J_{PH}$ and $^3J_{FH}$). Additional $^4J_{FH}$ coupling gives a clear septet structure to each component of the chlorophosphorane but only unresolved multiplets appear in the spectrum of the fluorophosphorane.

The $^{31}P\{^1H\}$ spectra of these two compounds at similar low temperatures are likewise unchanged from those at normal temperature; the ^{31}P spectrum of $CH_3(CF_3)_2PCl_2$ consists of a septet, arising from coupling of the phosphorus and six

Table IV. Mass Spectral Data for $CH_3(CF_3)_2PXY$

	Intensity[a]					
m/e	X = Cl Y = Cl	X = F Y = F	X = OCH_3 Y = OCH_3	X = F Y = OCH_3	X = F Y = $N(CH_3)_2$	Assignment[b]
228					0.18[c]	$CH_3(CF_3)_2PN(CH_3)_2$[c]
221	1.10					$CH_3(CF_3)_2P^{37}Cl$
219	3.25[c]			0.70		$CH_3(CF_3)_2P^{35}Cl$[c], $C_3F_7H_3PO$
215			6.58[c]	1.33[c]		$CH_3(CF_3)_2POCH_3$[c]
207		2.03			1.16	$(CF_3)_2PF_2$
203	0.98	3.91[c]		9.98[c]	3.72[c]	$CH_3(CF_3)_2P(F)$[c]
202					0.31	$CH_2(CF_3)_2PF$
200	0.54				1.25	$C_3F_5H_3P^{35}Cl$, $C_3F_6H_2NP$
189	0.10					$C_2H_3F_3P^{37}Cl_2$
187	0.60					$C_2H_3F_3P^{35}Cl^{37}Cl$
185	0.95					$C_2H_3F_3P^{35}Cl_2$
184	0.25[c]			1.20		$CH_3(CF_3)_2P$[c]
178					0.99	$C_4H_9F_4PN$
177			17.33			$C_4H_9F_3O_2P$
171	0.5					$C_2H_3F_4P^{37}Cl$
169	1.53			2.20		$(CF_3)_2P$, $C_2H_3F_4P^{35}Cl$
166				0.60		$C_3H_4F_5P$
165			4.85[c]	23.20		$C_3H_6F_4OP$[c]
158					3.18	$C_4H_8F_3PN$
157		11.70				CF_3PF_3
153	2.63	20.65		6.03	8.56	$C_2H_3F_5P$
152		1.40			0.61	$C_2H_2F_5P$
134			0.18	1.23	0.88	$C_2H_3F_4P$
131	4.80		1.21		7.47	C_2F_4P, $C_2H_6F_2O_2P$
127			11.79			$C_3H_9FO_2P$
128					1.38	$C_3H_9F_2PN$
121	0.91					CH_2F_4P
119	2.94	0.63		1.10	0.55	CF_4P
115			7.97[c]	17.86		$C_2H_6F_2OP$[c]
114					0.42	$C_2H_2F_3P$, CF_3PN
107		0.70				PF_4
103	4.40	22.75		5.90	11.19	CH_3F_3P
102		1.22			0.66	CH_2F_3P
101	1.17					CF_3PH
100	0.66				0.66	CF_3P
96				0.61		$C_2H_3F_2P$
94					0.66	C_2H_6FPN
93			8.31			$C_2H_6O_2P$
87	2.05					$FP^{37}Cl$
85	6.17					$FP^{35}Cl$
84		1.03		1.01		CH_3F_2P
83	1.12	1.03				CH_2F_2P
81	8.23		6.41	6.37	10.75	CF_2P
77			7.11			C_2H_6OP
69	15.35	23.10	6.41[c,d]	7.84	9.66	CF_3, PF_2
68						CH_6FP
67	0.85		0.17		2.19	CH_5FP
66					0.33	CH_4FP, H_2FNP
65	6.95	3.55	3.81	6.27	12.94	CH_3FP, $HFPN$
64		0.89		0.70	0.66	CH_2FP
63			4.16			CH_4OP
62			1.39		0.61	CFP
51					3.29	HFP, CHF_2
50		1.18		0.90	1.10	PF, CF_2
47	2.80		7.80	2.80	7.35	CH_4P, PO, H_2NP
46			1.39		0.44	CH_3P
45	2.44	1.88	3.12	2.10	0.66	CH_2P, C_2H_7N, C_2H_5O, PN
44		0.96				HCP
43					0.99	C_2H_5N, CP
42					1.14	C_2H_4N
41					1.03	C_2H_3N
38	4.90					$H^{37}Cl$
36	17.00					$H^{35}Cl$
35	1.47					^{35}Cl
32	1.45				0.39	PH
31	1.83	1.66			2.63	P, CF

[a] Intensities are expressed as percent total ionization summed over all ions with *m/e* greater than 30. [b] Reasonable structural formulas are quoted in some cases for ease of identification of species only. [c] Identity confirmed by mass measurement. [d] CF_3:PF_2 = 1.0:2.2.

equivalent F atoms of the CF_3 groups whereas that of $CH_3(CF_3)_2PF_2$ consists of a triplet of septets due to two equivalent directly bound F atoms and six F atoms in two equatorial CF_3 groups coupled to phosphorus.

The NMR spectral behavior of the monofluorophosphoranes $CH_3(CF_3)_2PFY$ [Y = OCH_3, $N(CH_3)_2$] suggest, in both cases, the ground-state structure B. The ^{19}F NMR spectra of the CF_3 regions at +33 °C (Y = OCH_3) or +69 °C [Y = N-

Table V. NMR Spectral Data for $CH_3(CF_3)_2PXY$

		Chem shifts				Coupling constants[d]								
Compd	Temp, °C	τ_H[a]	ϕ_{CF_3}[b]	ϕ_F[b]	δ_P[c]	$^1J_{PF}$	$^2J_{PF}$	$^2J_{PH}$	$^3J_{PH}$	$^3J_{FH}$	$^4J_{FH}$	$^3J_{FF}$	$^4J_{FF}$	$^5J_{FH}$
$CH_3(CF_3)_2PCl_2$	30	7.78[e]	75.4[f]		151.9[g,h]		134	10.3			0.7			
	−100		76.8		153.8[g,h]		133							
$CH_3(CF_3)_2PF_2$[y]	30	8.06[i]	66.9[j]	44.6[k]	148.3[g,l]	849	154	19.3		12.3	0.4	17.5		
	−100		66.4[j]		148.9[g,l]	840	154					16.5		
$CH_3(CF_3)_2P(OCH_3)_2$	30	8.30[n]	68.7[n]		173.4[g,h]		68.0	12.6						
		6.08[m]							13.5					
	−40		68.7[o]		173.8		68.5							
$CH_3(CF_3)_2P(F)OCH_3$	30	8.21[p]	69.5[o]	34.2[o]	152.3[e,g]	823	~90	13.8		11.0	0.8			
		6.22[m,q]							14.7		1.9			0.3
	−40		68.6[r,s]				125.0[s]					14.0	12.0	
			72.7[o,t]				~60.0[t]							
	−60				152.0[g,u]	817								
$CH_3(CF_3)_2P(F)N(CH_3)_2$	30	8.22[p]	65.6[v]	12.9[n]	165.7[g,n]	756	81.5	14.7[x]		11.7[x]	0.9	16.0		
		7.07[p,w]							11.0		2.8			0.5
	−40		64.8[r,s]				122.5[s]					14.0		
			64.0[o,t]				~35[t]							
	−60				164.2[g,u]	756								

[a] τ in ppm relative to TMS ($\tau = 10.0$). [b] ϕ in ppm from $CFCl_3$ as internal standard with positive values indicating resonance to high field of standard. [c] δ in ppm from P_4O_6 capillary, positive values indicating resonance to high-field of standard. The chemical shift of 85% H_3PO_4 is +112 ppm vs. P_4O_6: A. C. Chapman, J. Homer, D. J. Mowthorpe, and K. T. Jones, *Chem. Commun.*, 121 (1965). [d] In Hz. [e] Doublet of septets. [f] Doublet of quartets. [g] $^{31}P\{^1H\}$ spectrum. [h] Septet. [i] Doublet of triplets of septets. [j] Doublet of triplets of unresolved multiplets. [k] Doublet of septets of quartets. [l] Triplet of septets. [m] OCH_3 group. [n] Doublet of partly resolved multiplets. [o] Broad doublet. [p] Doublet of doublet of septets. [q] Doublet of doublet of partly resolved multiplets. [r] Doublet of doublet of quartets. [s] Equatorial CF_3 group. [t] Axial CF_3 group. [u] Doublet of quartets of quartets. [v] At +33 °C the ^{19}F spectrum consisted of a relatively sharp doublet with a broad hump to higher field. At +90 °C (in C_6F_6) a doublet of doublets was observed, with the high-field member being significantly broader than the low-field member. Only $^2J_{PF}$ and $^3J_{PF}$ couplings were observed. [w] $N(CH_3)_2$ group. [x] The alternative assignment $^2J_{PH}$ (11.7 Hz) and $^3J_{FH}$ (14.7 Hz) would be equally valid because the overlapping spectrum does not permit a distinction; however, the assignment in the table is favored because of the similarity of coupling constants to those of related systems. [y] Our chemical shift and coupling constant values given herein are in essential agreement with those of Sawin[5] except for the ^{31}P chemical shift of $CH_3(CF_3)_2PF_2$ which, when converted to the P_4O_6 scale, was given as 137.1 ppm.

$(CH_3)_2]$ consist of a doublet of doublets. Cooling the samples resulted in a collapse of the CF_3 portion of the spectrum in both cases with eventual clear separation of the signals at moderate temperatures (~−40 °C) into two chemically shifted regions of equal intensity consisting respectively of a well-spaced double doublet of quartets with a large value of $^2J_{PF}$ and an overlapping, poorly resolved doublet of quartets which results from the much smaller relative value of $^2J_{PF}$. The approximate coalescence temperatures are +20 °C [Y = $N(CH_3)_2$] and −20 °C (Y = OCH_3). Therefore both compounds possess the ground-state structure B in which one CF_3 occupies an axial location (characterized by a small $^2J_{PF}$ value)[3] and the other CF_3 group occupies an equatorial location (characterized by a relatively large $^2J_{PF}$ value)[3] in the trigonal bipyramid. It is also notable that the equatorial CF_3 group, which is cis to the axial fluorine in B exhibits a large $^3J_{PF}$ coupling whereas the $^3J_{PF}$ coupling between the axial CF_3 groups and the (trans) axial F appears to be very small or zero.

The presence of nonequivalent CF_3 groups in $CH_3(CF_3)_2PFY$ is also clearly demonstrated by low-temperature $^{31}P\{^1H\}$ NMR spectroscopy. In both cases [Y = OCH_3, $N(CH_3)_2$] the signal was split into a major doublet as a result of coupling with the single fluorine and each component was further split into quartets of quartets as the result of coupling to the fluorine atoms in two distinct CF_3 groups. The quartet separations are in excellent agreement with the $^2J_{PF}$ values obtained from the ^{19}F spectra.

The NMR data show clearly that the most electronegative ligand, F, occupies the axial site in keeping with preference rule first enunciated by Muetterties et al.[20] and the OCH_3, $N(CH_3)_2$, and CH_3 groups preferentially occupy equatorial sites.[20,23] The CF_3 groups are distributed between the remaining available locations which are necessarily nonequivalent in B in keeping with the apicophilic or axial preference series:[1-3] F, (Cl) > CF_3 > OCH_3, $N(CH_3)_2$, CH_3. Groups separated by a comma cannot be ranked relative to one another on the basis of available data. The present series also does not permit an unambiguous placement of Cl, hence the parentheses; however the similarity of the NMR parameters of $CH_3(CF_3)_2PCl_2$ and $CH_3(CF_3)_2PF_2$, as discussed earlier, strongly suggests, in keeping with previous evidence,[1-3] that Cl preferentially occupies an axial environment relative to CF_3, a conclusion which is at variance with those derived from vibrational studies of related compounds.[24] The position of Cl indicates that the axial preference series is not wholly governed by the electronegativity of the substituent. It is further notable that $CH_3(CF_3)_2P(F)N(CH_3)_2$ appears to have a higher barrier to CF_3 positional interchange than $CH_3(CF_3)_2P(F)OCH_3$ since less cooling of the sample is required to distinguish the CF_3 environments in the former.

The ^1H NMR spectra of $CH_3(CF_3)_2P(OCH_3)_2$ and $CH_3(CF_3)_2P[N(CH_3)_2]F$ under similar conditions show two chemically shifted regions in a 2:1 intensity ratio arising respectively from two OCH_3 groups or the $N(CH_3)_2$ group and the CH_3 group attached to phosphorus. The spectrum of $CH_3(CF_3)_2P(OCH_3)F$ shows two chemically shifted regions in a 1:1 intensity ratio arising from the OCH_3 and P–CH_3 functions. Both regions in the ^1H spectrum of $CH_3(CF_3)_2P(OCH_3)_2$ consist of a doublet of septets and in the cases of $CH_3(CF_3)_2PFY$ [Y = OCH_3, $N(CH_3)_2$] both regions consist of a double doublet of multiplets. In all three cases the major doublet is due to $^2J_{PH}$ or $^3J_{PH}$, and in the latter two cases the minor doublet arises from $^3J_{HF}$ or $^4J_{HF}$, coupling of the CH_3 protons of both types of CH_3 group with the directly bound F atom, and the remaining septet or multiplet fine structure which appears in all three cases arises from $^4J_{HF}$ or $^5J_{HF}$ coupling of the protons with the six F atoms in the equivalent CF_3 groups.

Magnetic Nonequivalence of Individual Fluorine Atoms in (Axial) CF_3 Groups. The ^{19}F NMR spectral behavior of $CH_3(CF_3)_2P(OCH_3)_2$ is rather unusual (Figure 2) since the doublet trifluoromethyl resonance exhibited by this compound at room temperature which is characterized by the rather low value of $^2J_{PF}$ of 68.0 Hz broadens as the temperature decreases,

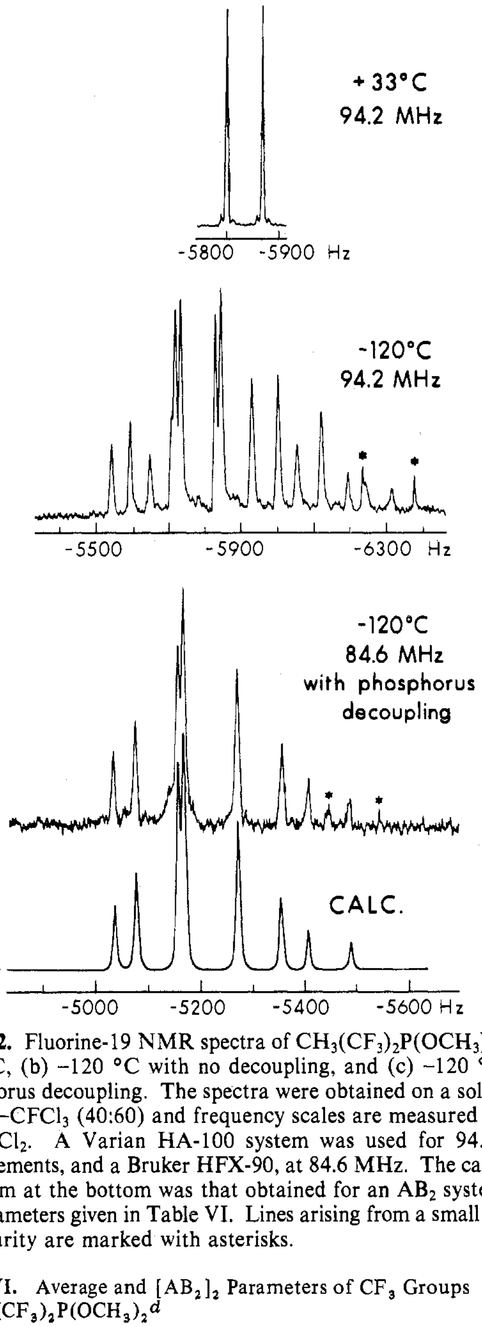

Figure 2. Fluorine-19 NMR spectra of $CH_3(CF_3)_2P(OCH_3)_2$ at (a) +33 °C, (b) −120 °C with no decoupling, and (c) −120 °C with phosphorus decoupling. The spectra were obtained on a solution in CF_2Cl_2–$CFCl_3$ (40:60) and frequency scales are measured relative to CF_2Cl_2. A Varian HA-100 system was used for 94.2-MHz measurements, and a Bruker HFX-90, at 84.6 MHz. The calculated spectrum at the bottom was that obtained for an AB_2 system with the parameters given in Table VI. Lines arising from a small amount of impurity are marked with asterisks.

Table VI. Average and $[AB_2]_2$ Parameters of CF_3 Groups in $CH_3(CF_3)_2P(OCH_3)_2$[d]

Temp, °C	ϕ_{F_A}[a]	ϕ_{F_B}[a]	$\Delta\nu$	$^2J_{PF_A}$	$^2J_{PF_B}$	$^2J_{AB}$	$^2J_{AB}/\Delta\nu$
+30	68.7[b]			68.0[b]			
−120	70.0	67.3	234[c]	48.5	75.5	112.3	0.48

[a] Vs. $CFCl_3$: measured vs. CF_2Cl_2 and converted to $CFCl_3$ scale by adding +6.8 ppm. [b] Average value. [c] At 84.6 MHz. [d] ϕ values in ppm; $\Delta\nu$ and J values in Hz.

and eventually, at −120 °C, the signal splits into 16 detectable separate resonances spread over 500 Hz. Irradiation at ^{31}P resonance frequency transformed the 16-line grouping to an 8-line pattern, which can be satisfactorily analyzed[25,26] as an AB_2 system with parameters given in Table VI. Note that the weighted average of $^2J_{PF_A}$ and $^2J_{PF_B}$ at −120 °C (66.5 Hz) is in good agreement with the value of $^2J_{PCF}$ obtained at ordinary temperatures suggesting that the observed phenomenon arises from the removal of the normal equivalence of F atoms within the (axial) CF_3 groups of the molecule and also confirming that the signs of $^2J_{PF_{ax}}$ and $^2J_{PF_{eq}}$ are the same. The magnitude of $^2J_{F_AF_B}$ is similar to that obtained for a series of hindered CF_3-substituted aliphatic carbon compounds.[28] In addition, the weighted average of chemical shifts for F_A and F_B nuclei (68.2 ppm) agrees well with the averaged value observed at +30 °C again suggesting removal of chemical equivalence. The spectra are therefore consistent with the ground-state structure C, analogous to the postulated ground-state structures of $(CF_3)_3P(OCH_3)_2$,[1] $(CF_3)_3P[N(CH_3)_2]_2$,[1,2b] and $(CF_3)_3P[OSi(CH_3)_3]_2$.[27] The simplicity of the substituent groups in the present case (OCH_3) and coincident good fortune have allowed the analysis of the complex low-temperature spectra in contrast to the earlier cases[1,2,27] in which the very low-temperature spectra were so complex that they could not be analyzed. The $^{31}P\{^1H\}$ spectra of $CH_3(CF_3)_2P(OCH_3)_2$ at −120 °C (Figure 3) show a quintet of triplets confirming that the six fluorines in two CF_3 groups can be divided into two groups of magnetically nonequivalent F atoms in the relative proportions 4:2 in complete agreement with the analysis of the ^{19}F spectrum.

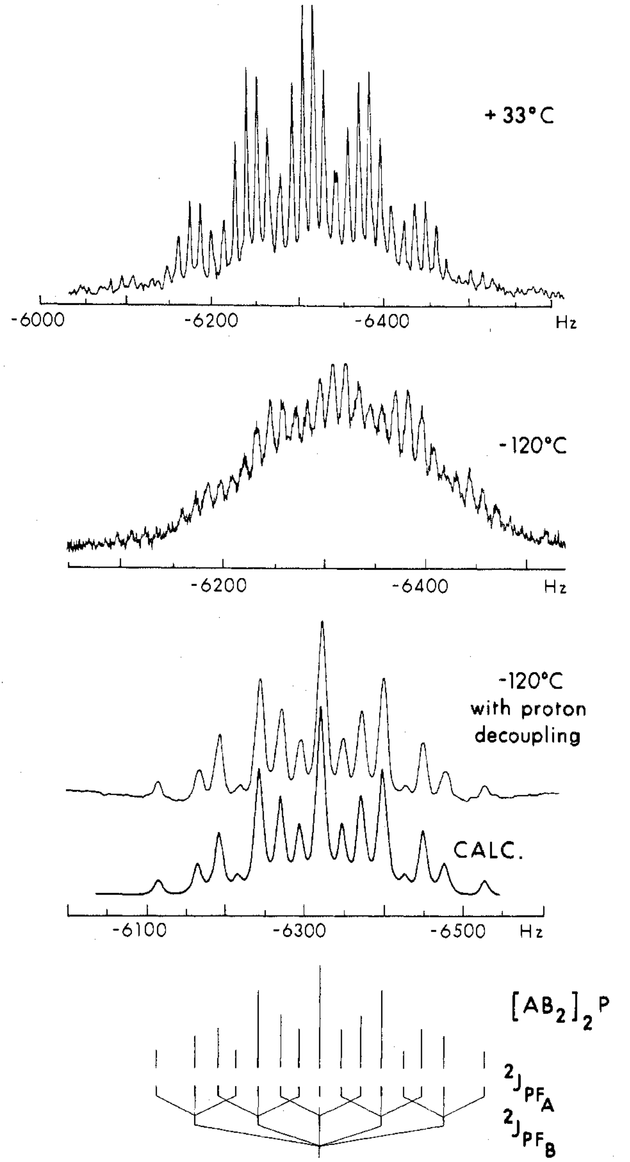

Figure 3. Phosphorus-31 FT NMR spectra of $CH_3(CF_3)_2P(OCH_3)_2$ at (a) +33 °C, (b) −120 °C with no decoupling, and (c) −120 °C with proton decoupling. The spectra were obtained on a solution of CF_2Cl_2–$CFCl_3$ (40:60) at 36.4 MHz and frequency scales are measured relative to P_4O_6 by means of the heteronuclear lock system of the Bruker HFX-90. The stick diagram at the bottom shows the origin of the splittings arising from the $[AB_2]_2$ fluorine spin system at −120 °C.

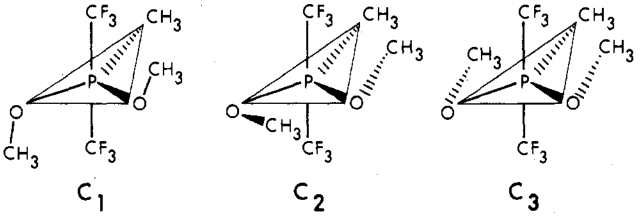

Figure 4. Possible orientations of OCH_3 groups with respect to the trigonal plane in $CH_3(CF_3)_2P(OCH_3)_2$.

Although various structures are possible for $CH_3(CF_3)_2P(OCH_3)_2$, all seem less likely than structure C in which two OCH_3 groups occupy equatorial substituent positions in the trigonal bipyramid. At low temperature however it appears that the rotation around the P–O bond ceases allowing the two OCH_3 groups to adopt fixed orientations relative to one another and to the CF_3 groups and the resultant interference destroys the equivalence of the F atoms within the CF_3 group as the result of some kind of "cogwheel" interaction mechanism. Several possibilities can be proposed. The methoxy CH_3 groups lie either above and below the equatorial plane (i.e., structure C1, Figure 4) or in the equatorial plane in the two different relative orientations (structures C2 or C3). Since the CF_3 group is relatively bulky and since axial substituents seem to lead to greater molecular crowding when space-filling molecular models are constructed, the C2 structure with the OCH_3 group lying in the plane might be the most likely but any conclusion at this stage is purely speculative.

Experimental Section

All reactions were done in sealed tubes and standard vacuum techniques were used throughout. $(CH_3)_3SiN(CH_3)_2$,[29] $(CH_3)_3SiOCH_3$,[30] and $(CH_3)_3SiSCH_3$[31] were prepared by published methods. $CH_3P(CF_3)_2$ was prepared by several methods[32,33] and spectrally characterized by comparison with literature properties.[8,9,14] Commercial SbF_3 (Alfa) was vacuum-sublimed twice before use to reduce oxide and water impurities which yield phosphine oxides during fluorinations. Dimethylamine, $(CH_3)_4Sn$ (Alfa), and Cl_2 (Matheson) were used without further purification.

Preparation of Methylbis(trifluoromethyl)dichlorophosphorane. $CH_3(CF_3)_2P$ (0.652 g, 3.54 mmol) and chlorine (0.315 g, 17.14 mmol) reacted smoothly upon warming slowly from −196 °C to room temperature to yield $CH_3(CF_3)_2PCl_2$ (0.900 g, 3.53 mmol) which was trapped at −45 °C and separated from more volatile unreacted Cl_2 (0.966 g, 13.60 mmol).

Preparation of Methylbis(trifluoromethyl)difluorophosphorane. (a) Shaking $CH_3(CF_3)_2PCl_2$ (1.640 g, 6.43 mmol) with excess resublimed antimony trifluoride for 16 h at room temperature gave $CH_3(CF_3)_2PO$ (0.072 g, 0.40 mmol, 6%) which was trapped at −45 °C and $CH_3(CF_3)_2PF_2$ (1.164 g, 5.24 mmol, 80%) which was trapped at −78 °C.

(b) Treating $(CF_3)_2PF_3$ (1.07 g, 4.73 mmol) with tetramethyltin (0.554 g, 3.10 mmol) for 18 h at room temperature resulted in a slow reaction with formation of a white solid. Separation of the volatile products under vacuum gave $CH_3(CF_3)_2PF_2$[5] (0.582 g, 2.62 mmol, 85% yield), unreacted $(CH_3)_4Sn$ (0.061 g, 0.51 mmol), and unreacted $(CF_3)_2PF_3$ (0.180 g, 0.80 mmol). The white solid residue dissolved in CD_3CN and gave signals consistent with $[(CH_3)_3Sn][(CF_3)_2PF_4]$.[6]

Reaction of Methylbis(trifluoromethyl)difluorophosphorane with Dimethylamine. Preparation of $CH_3(CF_3)_2P(F)N(CH_3)_2$. $CH_3(CF_3)_2PF_2$ (0.358 g, 1.61 mmol) and a deficiency of $(CH_3)_2NH$ (0.100 g, 2.22 mmol) reacted immediately on contact at room temperature with formation of a white solid material. The only volatile product obtained was $CH_3(CF_3)_2P(F)N(CH_3)_2$ (0.357 g, 1.45 mmol, 90% yield). A reaction under similar conditions with a large excess of dimethylamine gave only $CH_3(CF_3)_2P(F)N(CH_3)_2$ and no detectable bis(dimethylamino)phosphorane. Under more severe conditions, $CH_3(CF_3)_2PF_2$ reacted with excess dimethylamine to give only $CH_3(CF_3)_2P(F)N(CH_3)_2$ and the pyrolysis products of the latter. The separate pyrolysis of the monofluoride is described below.

Reaction of Methylbis(trifluoromethyl)difluorophosphorane with (Dimethylamino)trimethylsilane. Treatment of $CH_3(CF_3)_2PF_2$ (0.388 g, 1.75 mmol) with $(CH_3)_3SiN(CH_3)_2$ (0.144 g, 1.23 mmol) gave $CH_3(CF_3)_2P(F)N(CH_3)_2$ (0.307 g, 1.24 mmol, 100% yield based on available $(CH_3)_3SiN(CH_3)_2$), unreacted $CH_3(CF_3)_2PF_2$ (0.111 g, 0.50 mmol), and slightly impure $(CH_3)_3SiF$ (0.118 g, ~1.26 mmol).

Preparation of Methylbis(trifluoromethyl)dimethoxyphosphorane. (a) $CH_3(CF_3)_2PCl_2$ (0.190 g, 0.74 mmol), $(CH_3)_3SiOCH_3$ (0.173 g, 1.80 mmol), and a catalytic amount of iodine were combined in a sealed tube at −196 °C and allowed to warm slowly to room temperature with shaking. Separation of the products under vacuum gave $CH_3(CF_3)_2P(OCH_3)_2$ (0.158 g, 0.64 mmol, ~90%) which trapped at −45 °C, $CH_3(CF_3)_2P(O)$ (0.021 g, 0.09 mmol, ~10%), and an unseparated mixture of $(CH_3)_3SiCl$ and unreacted $(CH_3)_3SiOCH_3$ (0.84 g) which trapped at −196 °C.

(b) A mixture of $CH_3(CF_3)_2PCl_2$ (0.478 g, 1.88 mmol) and $(CH_3)_3SiOCH_3$ (0.536 g, 5.15 mmol) reacted on warming slowly from −196 °C to room temperature, to give a mixture of $CH_3(CF_3)_2P(OCH_3)_2$ and $(CF_3)_2P(O)CH_3$ (0.414 g total with an approximately 1:1 molar ratio as indicated by the ^{19}F NMR spectrum) in the least volatile fractions. A mixture of $(CH_3)_3SiCl$ and unreacted $(CH_3)_3SiOCH_3$ (0.537 g) was trapped at −112 °C and CH_3Cl (0.045 g, 0.99 mmol) was trapped at −196 °C.

Preparation of Methylbis(trifluoromethyl)fluoromethoxyphosphorane. $(CF_3)_2P(CH_3)F_2$ (0.377 g, 1.69 mmol) and $(CH_3)_3SiOCH_3$ (0.190 g, 1.82 mmol) were combined in a sealed tube at −196 °C and allowed to warm slowly with shaking to room temperature. Separation of the products gave $CH_3(CF_3)_2P(OCH_3)F$ (0.393 g, 1.67 mmol, 100%) which was trapped at −63 °C and a more volatile mixture of $(CH_3)_3SiF$ and unreacted $(CH_3)_3SiOCH_3$ (0.183 g).

Reaction of $CH_3(CF_3)_2P$ with NO_2. $CH_3(CF_3)_2P$ (0.160 g, 0.87 mmol) and NO_2 (0.044 g, 0.96 mmol) were allowed to react at room temperature for 16 h in a sealed tube. Separation of the volatile products under vacuum yielded $CH_3(CF_3)_2PO$ (0.174 g, 0.87 mmol, 100% yield), identified by comparison of infrared and NMR parameters with literature values,[8,9] and a mixture of NO and unreacted NO_2 (0.030 g).

Pyrolysis of $CH_3(CF_3)_2P(F)N(CH_3)_2$. Heating $CH_3(CF_3)_2P(F)N(CH_3)_2$ (0.276 g, 1.17 mmol) in a sealed tube for 20 h at 70 °C gave the following volatile products: CF_3H (0.057 g, 0.81 mmol) and $CH_3(CF_3)PF_2N(CH_3)_2$ (0.063 g, 0.32 mmol) identified by comparison of NMR and infrared spectral properties with those of a well-characterized sample.[17] An unidentified volatile solid (0.022 g) was also obtained and a quantity of an involatile liquid containing $CF_3(CH_3)P$ structural groups remained in the reaction vessel (0.134 g).

Attempted Reaction of $CH_3(CF_3)_2PF_2$ and $(CH_3)_3SiSCH_3$. $CH_3(CF_3)_2PF_2$ (0.266 g, 1.20 mmol) and $(CH_3)_3SiSCH_3$ (0.336 g, 2.80 mmol) were combined in a sealed NMR tube. No reaction took place as indicated by the unchanged NMR spectrum of the mixture after standing at room temperature for 7 days. A similar reaction was also attempted in the presence of a trace amount of iodine with no success.

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Registry No. $CH_3(CF_3)_2PCl_2$, 51874-45-4; $CH_3(CF_3)_2PF_2$, 51874-46-5; $CH_3(CF_3)_2P(OCH_3)_2$, 51874-48-7; $CH_3(CF_3)_2P(F)OCH_3$, 51874-44-3; $CH_3(CF_3)_2P(F)N(CH_3)_2$, 51888-43-8; $CH_3(CF_3)_2P$, 1605-54-5; $(CH_3)_2NH$, 124-40-3; $(CH_3)_3SiN(CH_3)_2$, 2083-91-2; $(CH_3)_3SiOCH_3$, 3219-63-4; $CH_3(CF_3)_2P(O)$, 677-73-6; $(CF_3)_2PF_3$, 1184-82-3; NO_2, 10102-44-0; CF_3H, 75-46-7; $CH_3(CF_3)PF_2N(CH_3)_2$, 61916-01-6.

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Coordination Chemistry of Imidazole Derivatives. A Search for Carbon-Bound Chelates with First-Row Transition Metal Ions

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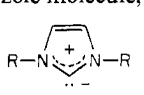
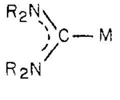
Structural conclusions about complex ions formed from several imidazole derivatives, from which chelates could result if carbon–metal bonding occurred, have been deduced from NMR data and electronic absorption spectra. None of the ligands examined show evidence of formation of carbon-bound chelates with Co(II) or Cu(II). Less extensive studies with Ni(II) and Fe(II) also gave no evidence of carbon-bound species. Two crystalline substances, dichlorobis[1-(2-pyridylmethyl)benzimidazole]cobalt and dichlorobis[1-(2-pyridylmethyl)-4,5-dimethylimidazole]cobalt were examined by x-ray diffraction. Dichlorobis[1-(2-pyridylmethyl)benzimidazole]cobalt crystallized from acetonitrile as blue crystals in the space group $P\bar{1}$ with $Z = 2$, $a = 10.314$ (3) Å, $b = 11.458$ (2) Å, $c = 12.442$ (4) Å, $\alpha = 63.37$ (2)°, $\beta = 74.58$ (2)°, $\gamma = 82.17$ (2)°, $\rho_{\text{calcd}} = 1.45$ g cm^{-3}, and $\rho_{\text{obsd}} = 1.43$ g cm^{-3}. Least-squares refinement of 2600 independent reflections with $F^2 \geq 3\sigma(F^2)$ gave a conventional R factor of 0.030. Dichlorobis[1-(2-pyridylmethyl)-4,5-dimethylimidazole]cobalt crystallized from Me_2SO-d_6 as blue crystals in the space group $P2_1/c$ with $Z = 4$, $a = 8.343$ (2) Å, $b = 16.982$ (3) Å, $c = 19.297$ (4) Å, $\beta = 117.35$ (2)°, $\rho_{\text{calcd}} = 1.38$ g cm^{-3}, and $\rho_{\text{obsd}} = 1.39$ g cm^{-3}. Least-squares refinement of 3121 independent reflections with $F^2 \geq 3\sigma(F^2)$ gave a conventional R factor of 0.036. In both cases, the Co^{2+} ion was tetrahedrally coordinated by Cl^- ions and by two organic ligands coordinated via the imidazole nitrogen in agreement with the conclusions drawn from solution data.

The imidazolium ylide has been identified as a ligand which can complex with transition metal ions via the carbon atom C(2). The parent imidazole molecule, R = H, has been shown

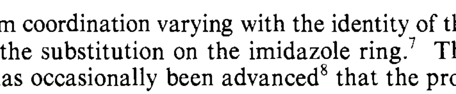


to complex in this manner with Ru(II) and Ru(III).[1] The 1,3-dimethyl derivative ($R = CH_3$) gives carbon-bound structures with Fe(0) and Cr(0) in carbonyl species.[2] The 1,3-diphenyl derivative forms a carbon-bound complex with Hg(II).[3] Histidine forms a carbon-bound complex with Ru(II) and Ru(III).[4] This mode of bonding can be viewed as a type of metal–carbene complexation and is therefore related structurally to carbon-bound amidinium species.[5]



Among the metal ion centers which form stable complexes of this type are Cr, Fe, Mn, Co, and Ni, although the majority of the reported examples involve the heavier transition metals. Some[6] of the iron complexes are in the formal II oxidation state.

In view of the importance of the imidazole ring of histidine as a metal ion binding site in metalloenzymes,[7] it is of interest to know the limiting conditions for formation of carbon-bound complexes of imidazole. It is clear from a variety of synthetic, spectroscopic, and crystallographic studies that the first-row transition metal ions usually form bonds with imidazole and its simple alkyl derivatives via the pyridine nitrogen, the



maximum coordination varying with the identity of the metal ion and the substitution on the imidazole ring.[7] The proposition has occasionally been advanced[8] that the protonated nitrogen is also a metal-binding site but this seems unlikely and has not been demonstrated to occur.[7,9] Shepherd[10] has studied Fe(II) and Fe(III) complexes with simple imidazole derivatives and histidine in mixed complexes with cyanide ion and found no evidence for complexation via C(2).

As a further step toward defining the limits in which carbon complexation of the imidazole ring is feasible, we have studied ligands **1**–**9** in which a chelation could occur if bond formation occurred at C(2) of the imidazole ring. Complexes of these ligands with Co(II), Cu(II), Ni(II), and Fe(II) were studied