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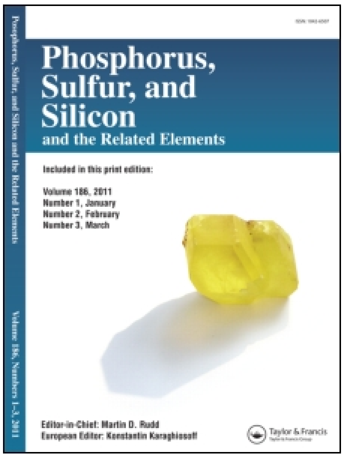

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Neutral six-coordinate fluoro-phosphorus compounds

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NEUTRAL SIX-COORDINATE FLUORO-PHOSPHORUS COMPOUNDS

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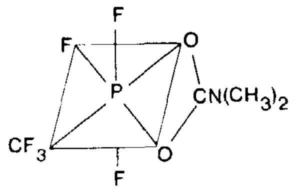
Abstract Three new six-coordinate trifluoromethylfluorophosphorus carbamates $F_{4-n}(CF_3)_nPO_2CN(CH_3)_2$ (n = 1, 2, 3) have been prepared by reaction of trimethylsilylcarbamate with the appropriate fluorophosphorane. All products appear to be six-coordinate as indicated by characteristic high field ^{31}P nmr chemical shifts and in some cases are fluxional. Two isomers are observed in the nmr spectra of the compound with n = 1. Only one structure is formed in the n = 2 and 3 cases. The crystal and molecular structure of $F(CF_3)_3PO_2CN(CH_3)_2$ revealed a six-coordinate structure with the unique F in the plane containing the chelated carbamate.

Only a few neutral six-coordinate compounds of phosphorus are known, some of which have been structurally characterized.[1-2] Following our initial synthesis[3] by means of "insertion" of CE_2 (E = O, S) into the P-N bond of $CH_3(CF_3)_3PN(CH_3)_2$[4] and further study of the reaction pathway,[5] we developed a generally useful method for synthesis of fluorophosphorus carbamates by means of the reaction of trimethylsilylcarbamate with a phosphorus(V) halide. In the case of the trifluoromethylfluorophosphoranes $(CF_3)_nPF_{5-n}$ (n = 1,2,3), (eq 1), reactions proceeded smoothly in evacuated sealed tubes at moderate temperatures to give three new, monocarbamato derivatives (I, n=1), (II, n=2), and (III, n=3) in good yield. All of the

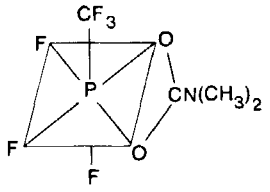
$$(CF_3)_nPF_{5-n} + (CH_3)_3SiO_2CN(CH_3)_2 \longrightarrow F_{4-n}(CF_3)_nPO_2CN(CH_3)_2 + (CH_3)_3SiF \qquad (1)$$

compounds are crystalline solids [m.p.: **I** (58°), **II** (97°) and **III** (61°)] with high-field ^{31}P nmr chemical shifts (135 to 149 ppm vs H_3PO_4) indicative of a six-coordinate phosphorus centre.

The ^{19}F (and ^{31}P) nmr spectra of (**I**) indicate that it is fluxional at ordinary temperatures as was the first carbamate that we synthesised, $CH_3(CF_3)_3PO_2CN(CH_3)_2$.[3] At 250°K, two isomeric structures of **I** are visible in the nmr spectra in 2:1 relative proportions. Each shows the characteristic nmr spectral properties of a six-coordinate phosphorus carbamate thus the two species are assigned to the two possible geometrical isomers A and B



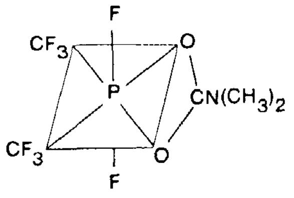
I-A



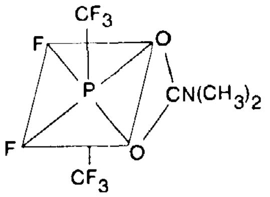
I-B

Principal nmr spectral parameters are given in the table. Using the crystal structure of **III** as a guide, we can associate high field fluorine atom shifts with "equatorial" positioning and speculatively propose that the dominant isomer is **I**-B.

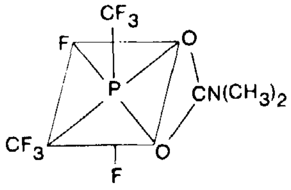
Compound **II** shows a first order spectrum at all temperatures suggesting that only one isomer exists (although here three are possible) or that the compound is still fluxional at the lowest temperature yet investigated (223° K).



II-A



II-B



II-C

We presently favour the interpretation of the spectrum in terms of one unique structure because (a) there is no evidence of line broadening at the lowest temperature in the nmr spectra and (b) the generally facile resolution of the fluxional behaviour of all the

Principal NMR Spectral Parameters for the Carbamates

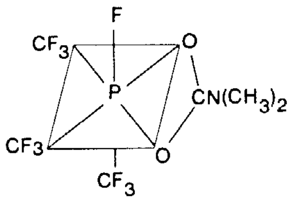
Compound	$\sigma_{^{31}P}$[a]	ϕ_{CF_3}[b]	ϕ_F[b]	$^1J_{PF}$ (Hz)	$^2J_{PCF}$ (Hz)
I-B (2)	145.0				145.0
		69.7	85.1[d]	954.0[d]	
			58.9[e]	830.7[e]	
I-A (1)	133.9	70.4			155.6
			84.0[d]	921.5[d]	
			59.6[e]	936.3[e]	
II	146.0[f]	70.0[g]			164.3
			90.9[h]	1057.2	
III[i]	148.5	69.1(1)[d]			97.5[d]
		68.8(2)[e]	103.7	99.74	141.5[e]

a) ppm vs 85% H_3PO_4, positive values to high field.
b) ppm vs $CFCl_3$, positive values to high field.
c) NMR parameters obtained at -30° except where noted otherwise.
d) "equatorial" (i.e., in same plane as the carbamate ligand).
e) "axial" (i.e., perpendicular to the carbamate-phosphorus plane).
f) Triplet of septets at 30°, also triplet of septets at -50°.
g) At +32° a doublet of triplets, same at -50°.
h) At +32° a broad doublet, a doublet of septets from +10° to -50°.
i) ^{19}F nmr shifts obtained at -50°C. ^1H is a doublet at -40° (τ: 7.19, 7.21), a singlet at +32°. ^{31}P (obtained at -50°) gives J values. Rel. intensity in brackets.

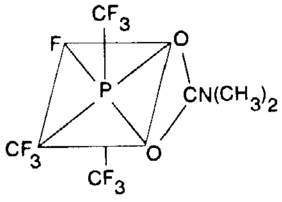
other compounds in the system at temperatures no lower than 250°K. The parameters (table) suggest that the species is isomer **II**-B with F atoms cis to each other in the plane of the carbamate ligand. The static spectrum of **II**-C we think is likely to be second order.

The third compound, **III**, which can form two isomers (**III**-A and **III**-B), is also fluxional at normal probe temperatures but at temperatures of the order of -40 to -60°C, the fluxionality has ceased and the ^{19}F and ^{31}P nmr spectra can be interpreted on a first order basis in terms of structure **III**-B. The proximity of CF_3

chemical shifts yields an accidental coincidence in the spectrum which is however separable at 376.5 MHz. Although the ^{19}F and ^{31}P spectra suggest that only one isomer is present, the presence of two proton signals at -40°C suggests that both isomers may be present in approximately equal proportions. An equally viable alternative is the assignment of the two proton signals in isomer B to the cis and trans oriented (with respect to the fluorine in the plane) CH_3 groups.



III-A



III-B

An X-ray structural determination of a single crystal of **III** revealed the six-coordinate structure with a chelated carbamate having the isomeric structure **III**-B. The principal bond lengths are: (in Å) P-F, 1.590; P-$O_{trans(F)}$, 1.778; P-$O_{cis(F)}$, 1.832. "Axial" P-C and "equatorial" P-C distances (av. P-C(F), 1.914) are not statistically distinguishable. The "axial" CF_3 groups are nearly linear (<CPC = 170.9°). The distortion from linearity is just a little larger than in the methyl carbamate.[3] As in the methyl carbamate[3] the carbamato ligand, P, the unique F and the carbon of one CF_3 are essentially coplanar. This structure supports the inequivalent environments of III-B as the source of the two proton signals.

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