Azido- and Thiocyanato-derivatives of Some Chlorofluorophosphate(V) Ions

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The preparation and characterisation of some solid tetra-ethylammonium chlorofluorophosphates(V), $[NEt_4]^+[PF_nCl_{6-n}]^-$ ($1 \leqslant n \leqslant 3$), the anions of which were previously known only in mixed systems, are described for the first time. Their reactions with suitable metal pseudohalides (LiN_3 or AgNCS) lead to substitution of the chlorine ligands only. In some instances ligand redistribution involving fluoride occurs. Some of the derivatives have also been prepared by ligand-exchange reactions between appropriate phosphate(V) anions. Several structural assignments have been made on the basis of the observed P–F splitting patterns and the pairwise additivity of ^{31}P n.m.r. shifts, although fluxional behaviour was observed in some cases. All the pseudohalogeno-species are unstable, the thiocyanato-compounds isolated as solids decomposing readily at room temperature.

Mixtures of chlorofluorophosphate $[PF_nCl_{6-n}]^-$ ions have been known in solution for some years,[1-5] and may be prepared, for example, by the reaction of PCl_5 with PF_5 in MeCN as solvent.[5] The individual ions, with the exception of *trans*-$[PF_2Cl_4]^-$, have been identified by ^{19}F and ^{31}P n.m.r. measurements.[5] The separate species have not been isolated hitherto in a pure state, however, although $[PF_2Cl_4]^-$ has been obtained in admixture with $[PF_6]^-$ as the caesium salt,[2] and the compound PCl_3F_2 has been reported to undergo conversion in the solid state into $[PCl_4]^+[PF_4Cl_2]^-$.[6] We present here relatively simple preparations of salts containing the ions $[PF_nCl_{6-n}]^-$, where $n = 1, 2$, or 3. Their reactions with LiN_3 or (for $n = 2$ or 3) AgNCS to give pseudohalogeno-derivatives have also been investigated. Substitution of the chlorine ligands only was found to occur. Azidofluorophosphates[7] and fluorothiocyanatophosphates[7,8] $[PF_{6-n}X_n]^-$ ($X = N_3$ or NCS; $1 \leqslant n \leqslant 3$) have been reported from the reaction of PF_5 with metal-azides or -thiocyanates in solution, the more highly substituted ($n > 1$) species being formed by disproportionation. Our results are in many cases complementary, since different starting materials and preparative routes have been used. N.m.r. evidence indicated that the thiocyanate ligand in these complexes is bonded through nitrogen,[8] as was deduced independently from i.r. data for the $[P(NCS)_6]^-$ ion, the preparation of which we have described very recently.[9] Evidence of ligand exchange between $[PF_6]^-$ and $[PX_6]^-$, where $X = N_3$ or NCS, and between $[PF_6]^-$ and $[PF_3(NCS)_3]^-$, is also presented. Stereochemical non-rigidity has been observed in some of the new species.

Experimental

All manipulations, including n.m.r. sample preparation, were carried out either under an inert atmosphere of dry nitrogen or *in vacuo*. Chemicals of the best available commercial grade were used, in general without further purification, except for tetra-alkylammonium chlorides which were dried as described previously,[9] and ammonium thiocyanate which was recrystallised from methanol. Lithium azide was prepared by the method of Hofman-Bang,[10] and anhydrous NEt_4NCS by reaction of equimolar amounts of NEt_4Br and NH_4NCS in methanol. The white precipitate of NH_4Br was filtered off and the solution then evaporated to dryness. The solid product was extracted several times with CH_2Cl_2, the resulting solution was evaporated under reduced pressure, and the solid freed of solvent by heating to 373 K *in vacuo* for 1 h.

Phosphorus-31 n.m.r. spectra were recorded at 307.2 K as described previously.[9] Chemical shifts were measured relative to external H_3PO_4, and are quoted with the downfield direction taken as positive. Carbon, H, N, P, and Cl microanalyses, and i.r. spectra, were obtained as described in earlier papers.[9,11,12] No attempt was made to isolate azido-species in view of their probable explosive nature.[11]

Tetraethylammonium Trichlorotrifluorophosphate, $[NEt_4][PF_3Cl_3]$.—An excess of PF_3 was passed into a solution of NEt_4Cl (2.9 g, 17.5 mmol) and Cl_2 (0.4 ml at 191 K) in CH_2Cl_2 at 243 K, until the green colour was discharged. The solvent was removed *in vacuo* and the resulting solid recrystallised from CH_2Cl_2 to give the *product* (1.45 g, 4.4 mmol). The remaining solution was treated with a third of its volume of CCl_4 and cooled to 253 K to give a further 1.4 g (Found: C, 29.7; H, 6.1; Cl, 32.3; N, 4.6; P, 9.0. $C_8H_{20}Cl_3F_3NP$ requires C, 29.6; H, 6.2; Cl, 32.8; N, 4.3; P, 9.5%). The ^{31}P n.m.r. spectrum (solvent CH_2Cl_2) showed a quartet due to the *fac* isomer, $\delta(^{31}P)$ −156.8, $^1J_{PF}$ 953 Hz (lit.,[5] δ −158.5, $^1J_{PF}$ 940 Hz), and a doublet of triplets due to the *mer* isomer, $\delta(^{31}P)$ −142.7, $^1J_{PF}$ 1 081 (t) and 970 Hz (d) (lit.,[5] $^1J_{PF}$ 1 060 and 950 Hz). The *fac* : *mer* ratio was estimated as *ca.* 3 : 1 from the peak intensities.

Tetraethylammonium cis-*Tetrachlorodifluorophosphate*, $[NEt_4][PF_2Cl_4]$.—PF_2Cl, prepared by the method of Cavell,[13] was added from a Rotaflo to equimolar quantities of NEt_4Cl and Cl_2 in CH_2Cl_2 at 243 K. Removal of the solvent and recrystallisation of the solid from CH_2Cl_2 gave the *salt* (Found: C, 28.3; H, 6.0; Cl, 39.5; N, 4.3; P, 9.0. $C_8H_{20}Cl_4F_2NP$ requires C, 28.2; H, 5.9; Cl, 41.6; N, 4.1, P, 9.1%). A sample of PF_2Cl sealed in a tube showed a triplet, $\delta(^{31}P)$ 175.7, $^1J_{PF}$ 1 369 Hz (lit.,[14] δ 176, $^1J_{PF}$ 1 380 Hz). The product $[NEt_4]$*cis*-$[PF_2Cl_4]$ in CH_2Cl_2 also gave a triplet, $\delta(^{31}P)$ −177.3, $^1J_{PF}$ 1 026 Hz (lit.,[5] δ −180, $^1J_{PF}$ 1 010 Hz).

Tetraethylammonium Pentachlorofluorophosphate, $[NEt_4][PFCl_5]$.—This compound was prepared as for $[NEt_4][PF_2Cl_4]$, but with $PFCl_2$ [15] as the phosphine. The *product* was insoluble in CH_2Cl_2 and was filtered off, washed with CH_2Cl_2, and dried at the pump (Found: C, 27.9; H, 6.2; Cl, 49.2; N, 3.2; P, 8.3. $C_8H_{20}Cl_5FNP$ requires C, 26.9; H, 5.6; Cl, 49.6; N, 3.9; P, 8.7%). The ^{31}P n.m.r. spectrum of $PFCl_2$ consisted of a doublet, δ 217.6, $^1J_{PF}$ 1 329 Hz (lit.,[16] δ 224, $^1J_{PF}$ 1 326 Hz), and that of $[NEt_4][PFCl_5]$ in $MeNO_2$ was also a doublet, at δ −223.2, $^1J_{PF}$ 1 054 Hz (lit.,[5] δ −224, $^1J_{PF}$ 1 050 Hz).

Tetraethylammonium Pentafluorothiocyanatophosphate, $[NEt_4][PF_5(NCS)]$.—An excess of PF_5 was passed into a

Table 1. Calculated and observed chemical shifts (δ values) and coupling constants (Hz) for $[PF_{6-n}X_n]^-$ in CH_2Cl_2

Ion	X = N_3			X = NCS		
	$\delta_{calc.}$	$\delta_{obs.}$	$^1J_{PF}$	$\delta_{calc.}$ [a]	$\delta_{obs.}$	$^1J_{PF}$
$[PX_6]^-$	[b]	−180.0		−261.2	−261.9	
$[PFX_5]^-$	[b]	−167.3	884	−232.9	−233.6	741
cis-$[PF_2X_4]^-$	−158.8	−158.5	851	−209.0	−209.5	750
trans-$[PF_2X_4]^-$	−154.8			−204.5		
fac-$[PF_3X_3]^-$	−152.1	−151.2	822	−189.7		
mer-$[PF_3X_3]^-$	−149.6			−185.2	−185.6	732
cis-$[PF_4X_2]^-$	−146.6			−170.4	−174.2	735
trans-$[PF_4X_2]^-$	−142.8			−165.9		
$[PF_5X]^-$	−147.2			−155.6	−154.2	735
$[PF_6]^-$	[b]	−145.1	718	−145.3	−145.1	718

[a] Values calculated by least squares fit of data. [b] Observed δ values used in calculation of additivity parameters.

CH_2Cl_2 solution of NEt_4NCS (1.59 g, 8.4 mmol) at 253 K. The solvent was removed *in vacuo* and the thermally unstable yellow solid was recrystallised from CH_2Cl_2 to give the *product* (2.5 g, 8.0 mmol) (Found: C, 35.0; H, 7.2; N, 8.9; P, 9.6. $C_9H_{20}F_5N_2PS$ requires C, 34.4; H, 6.4; N, 8.9; P, 9.9%); $\delta(^{31}P)$ (CH_2Cl_2) −154.2 (sextet, $^1J_{PF}$ 735 Hz) (see Results and Discussion section).

Tetraethylammonium Trifluorotrithiocyanatophosphate, $[NEt_4][PF_3(NCS)_3]$.—A small quantity of $[NEt_4][PF_3Cl_3]$ was treated with an excess of AgNCS in CH_2Cl_2 solution. The silver salts were removed by filtration, the residue was extracted with CH_2Cl_2, and the extract was combined with the filtrate. The resulting solution was evaporated to give a yellow *solid*. Insufficient material was obtained for phosphorus analysis (Found: C, 35.3; H, 6.2; N, 14.5. $C_{11}H_{20}F_3N_4PS_3$ requires C, 33.7; H, 5.1; N, 14.3%); $\delta(^{31}P)$ (CH_2Cl_2) −185.6 (quartet, $^1J_{PF}$ 732 Hz) (see Results and Discussion section).

Ligand-exchange Reactions involving $[PF_6]^-$.—Tetra-n-propylammonium hexafluorophosphate, $[NPr^n_4][PF_6]$, in CH_2Cl_2 solution was treated separately with solutions of $[N(C_5H_{11})_4][P(N_3)_6]$ [11] and $[N(n\text{-}C_5H_{11})_4][P(NCS)_6]$ [9] in the same solvent, prepared as described previously. The solution containing $[P(NCS)_6]^-$ was maintained at 243 K to prevent significant decomposition of the anion.[9] A similar reaction between $[PF_6]^-$ and $[PF_3(NCS)_3]^-$, prepared as described here, was also carried out.

Results and Discussion

(1) *Ligand Redistribution Reactions involving* $[PF_6]^-$.—(a) $[PF_6]^-/[P(N_3)_6]^-$ *exchange*. Ligand exchange between $[PF_6]^-$ and $[P(N_3)_6]^-$ was slow at room temperature. After 4 days the appearance of a new doublet in the ^{31}P n.m.r. spectrum at δ −167.3, $^1J_{PF}$ 884 Hz, indicated the presence of $[PF(N_3)_5]^-$ (Table 1). The spectrum changed very little, apart from a gradual increase in intensity of the doublet, but after 2 weeks a low intensity triplet (δ −158.5, $^1J_{PF}$ 851 Hz), ascribed to one of the isomers of $[PF_2(N_3)_4]^-$, was observed. More highly fluorinated derivatives such as $[PF_5(N_3)]^-$ were not detected. Several explanations for this behaviour are possible. First, since the chemical shifts of $[PF_4(N_3)_2]^-$ (both isomers) and $[PF_5(N_3)]^-$ are expected to be close to that of $[PF_6]^-$ (Table 1), strong bands from the latter may obscure any weak signals. These species could be particularly unstable with respect to loss of N_2 {as shown by the relative instabilities of $[PCl_5(N_3)]^-$ and $[PCl_4(N_3)_2]^-$ compared with $[P(N_3)_6]^-$},[11] although the absence of any fluoro-containing species in the decomposition products implies a different route to decomposition. {The decomposition products appeared to consist mainly of small amounts of $[NP(N_3)_2]_n$ with $n \geqslant 4$: [11] weak, broad resonances at −4.9 and −13.8 were detected.} Alternatively, the ion $[PF_5(N_3)]^-$ may be very unstable with respect to disproportionation. Support for this hypothesis is provided by ^{19}F n.m.r. evidence: even at 178 K the strongest resonances from the PF_5–N_3^- system were due to $[PF_6]^-$, and the two isomers both of $[PF_4(N_3)_2]^-$ and of $[PF_3(N_3)_3]^-$ were also detected.[7]

Since the assignment of the doublet to $[PF(N_3)_5]^-$ is unambiguous and the shifts of both $[PF_6]^-$ and $[P(N_3)_6]^-$ are known, the pairwise interaction method of Vladimiroff and Malinowski [5,9,11,17–20] may be used to calculate the shifts of all the members of the series $[PF_n(N_3)_{6-n}]^-$, with F : F, $N_3 : N_3$ and F : N_3 terms of −12.5, −15.1, and −11.8 p.p.m. respectively. The calculated values are shown in Table 1. Comparison with the experimental results strongly suggests that the isomer of $[PF_2(N_3)_4]^-$ observed in this reaction should be assigned a *cis* configuration. This is supported by its preparation by substitution into *cis*-$[PF_2Cl_4]^-$ [section 3(a)].

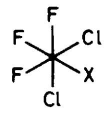
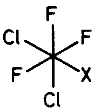
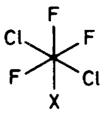
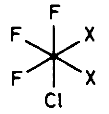
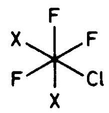
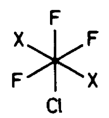
(b) $[PF_6]^-/[P(NCS)_6]^-$ *exchange*. Ligand redistribution between $[PF_6]^-$ and $[P(NCS)_6]^-$ was comparatively rapid. The initial ^{31}P n.m.r. spectrum showed a doublet (δ −233.6, $^1J_{PF}$ 741 Hz) to high frequency of the $[P(NCS)_6]^-$ resonance, readily assigned to $[PF(NCS)_5]^-$; after 1 day a 1 : 5 : 10 : 10 : 5 : 1 sextet (δ −154.2, $^1J_{PF}$ 735 Hz) and a 1 : 2 : 1 triplet (δ −209.5, $^1J_{PF}$ 760 Hz) were also observed. The data (together with results discussed in the following sections) and assignments are shown in Table 1; the pairwise parameters were originally evaluated from the shifts of $[PF_6]^-$, $[P(NCS)_6]^-$, and $[PF(NCS)_5]^-$, but were refined by a least squares best fit of the experimental data, giving NCS : NCS, F : F, and F : NCS terms of −21.77, −12.11, and −14.68 p.p.m., respectively. The triplet is assigned to *cis*-$[PF_2(NCS)_4]^-$ on the basis of the calculated shifts, as shown.

The sextet must be ascribed to $[PF_5(NCS)]^-$, which is clearly fluxional at the n.m.r. operating temperature. The peaks were sharp, suggesting that the process is rapid, whatever the mechanism of fluxionality. Interestingly, this ion appears not to be fluxional in CH_2Cl_2 or SO_2 at 203 K,[7] or in MeCN at 223 K,[8] since separate coupling constants of 725 Hz with the *cis* fluorines and 742 (CH_2Cl_2), 741 (SO_2), or 740 Hz (MeCN) with the *trans* fluorines were measured at these temperatures in the ^{19}F spectra. The ^{31}P n.m.r. spectrum at low temperatures should thus consist of a doublet of quintets. The reaction mixture was maintained at 243 K to reduce the risk of decomposition of thiocyanato-species, and low intensity signals which became apparent between δ −60 and −10 were not interpreted.

$[NEt_4][PF_5(NCS)]$ was prepared by the direct reaction of PF_5 and NEt_4NCS (Experimental section), and gave a ^{31}P n.m.r. spectrum identical with that just described. The chemical shift is in good agreement with the value (−156.4) reported for this ion in MeCN solution. The i.r. spectrum of a freshly prepared sample (Nujol mull) showed a strong absorption at 2 100 cm^{-1}, but after storage of the compound for 2 weeks at 243 K this band was totally absent, as a result of thermal instability.

Neither $[PF_4(NCS)_2]^-$ nor $[PF_3(NCS)_3]^-$ was detected in the ligand-exchange reaction. $[PF_3(NCS)_3]^-$ was prepared by the reaction of $[PF_3Cl_3]^-$ with an excess of AgNCS, and $[PF_4(NCS)_2]^-$ was observed as a product from exchange between $[PF_6]^-$ and $[PF_3(NCS)_3]^-$ [section 2(b)].

Table 2. Calculated and observed shifts (δ values) and coupling constants (Hz) for $[PF_3Cl_{3-n}X_n]^-$ ($1 \leqslant n \leqslant 3$)

		X = N_3			X = NCS		
Ion	Structure	$\delta_{calc.}$	$\delta_{obs.}$	$^1J_{PF}$	$\delta_{calc.}$	$\delta_{obs.}$	$^1J_{PF}$
$[PF_3Cl_2X]^-$		−140.7	−143.4	948 (d) 855 (t)	−167.1	−168.0	996 (d) 836 (t)
		−136.8			−155.7		
		−119.8			−146.4		
$[PF_3ClX_2]^-$		−138.6			−177.0	−179.0	1 039 (d) 869 (t)
		−134.7			−165.9		
		−134.6	−132.0	861 (d) 714 (t)	−172.8		
$[PF_3X_3]^-$	*fac*	−152.1			−189.7		
		−151.5 *	−151.2	822			
	mer	−149.6			−185.2	−185.6	732

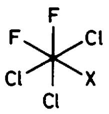
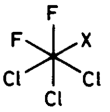
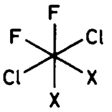
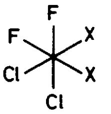
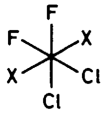
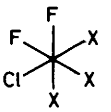
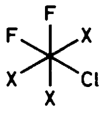
* Weighted average (assuming 3 : 1 *fac* : *mer* ratio).

(2) *Substitution into* $[PF_3Cl_3]^-$ *Ions*.—(a) *Azide*. The reaction of an excess of LiN_3 with the isomeric mixture of $[PF_3Cl_3]^-$ ions (Experimental section) led to a ^{31}P n.m.r. spectrum showing a simple 1 : 3 : 3 : 1 quartet pattern, which could arise from *fac*-$[PF_3(N_3)_3]^-$. No discrete resonances attributable to the *mer* isomer were detected. This could be due either to isomerisation to the facial form, or to fluxionality of *mer*-$[PF_3(N_3)_3]^-$, giving rise to a quartet which is not resolved from the signals of the *fac* isomer because of the expected similarities in chemical shift (Table 1), or to a rapid equilibration between the *fac*- and *mer*-forms. Such an equilibrium could lead to an averaging of the fluorine positions in the meridional isomer and of the chemical shifts. Indeed the weighted average of the calculated shifts (on the assumption of a 3 : 1 *fac* : *mer* ratio as in the starting material) agrees well with the observed shift. Both isomers of $[PF_3(N_3)_3]^-$ have been identified in the ^{19}F n.m.r. spectrum at 178 K from the reaction of PF_5 with N_3^- ions in CH_2Cl_2, but no ^{31}P data were reported.[7] The ^1J value at 307.2 K of 822 Hz (Table 1) is intermediate between that for the unique F in *mer*-$[PF_3(N_3)_3]^-$ and that for *fac*-$[PF_3(N_3)_3]^-$ at 178 K, which lends some support to the suggestion of a rapid equilibration between the isomers at the higher temperature. It is even possible on the basis of the coupling constants that the *mer*-isomer of $[PF_3(N_3)_3]^-$ is formed exclusively {as suggested by the results for $[PF_3Cl(N_3)_2]^-$; see later}, but if so it is evidently fluxional at 307.2 K. A variable-temperature study would be required to elucidate the position completely.

The addition of small quantities of LiN_3 to a CH_2Cl_2 solution of $[NEt_4][PF_3Cl_3]$ gave rise successively to two new doublets of triplets in the ^{31}P n.m.r. spectrum, assigned to isomers of $[PF_3Cl_2(N_3)]^-$ and $[PF_3Cl(N_3)_2]^-$, respectively (Table 2). The shifts of all the possible isomers of these species may also be calculated by the pairwise additivity method, as shown, since sufficient data are available from other systems for all the terms to be evaluated. Comparison of the experimental and calculated shifts indicates that $[PF_3Cl_2(N_3)]^-$ almost certainly has a facial arrangement of fluorines, which is reasonable in view of the higher initial concentration of *fac*-$[PF_3Cl_3]^-$ in the isomeric mixture. The structure of $[PF_3Cl(N_3)_2]^-$ cannot be assigned unambiguously on this basis, but it most probably has a meridional arrangement of F atoms, although there could be a dynamic equilibrium between the possible isomers, as suggested for $[PF_3(N_3)_3]^-$. A more negative chemical shift might then have been expected, however, in view of the calculated values.

The system containing $[PF_3Cl_{3-n}(N_3)_n]^-$ ions was unstable, and after 1 week an intense broad (*ca.* 800 Hz) resonance

Table 3. Calculated and observed chemical shifts (δ values) and coupling constants (Hz) for *cis*-$[PF_2Cl_{4-n}X_n]^-$ ($1 \leqslant n \leqslant 4$)

Ion	Structure	X = N_3			X = NCS		
		$\delta_{calc.}$	$\delta_{obs.}$	$^1J_{PF}$	$\delta_{calc.}$	$\delta_{obs.}$	$^1J_{PF}$
$[PF_2Cl_3X]^-$		−148.3			−183.2		
		−165.5	−161.7	910 (t)	−192.5		
$[PF_2Cl_2X_2]^-$		−128.7			−184.1		
		−146.0			−193.2	−194.0	757 (d) 1 029 (d)
		−145.8	−149.3	901 (t)	−200.3		
$[PF_2ClX_3]^-$		−143.7			−196.7		
		−143.7			−203.6	−204.5	655 (d) 887 (d)
cis-$[PF_2X_4]^-$		−158.8	−158.3	853 (t)	−209.0	−209.6	746 (t)

was apparent in the ^{31}P n.m.r. spectrum, centred at δ 0.9. No P–F coupling could be resolved in this region of the spectrum, indicating that the decomposition products are not polymeric fluorophosphazenes $(NPF_2)_n$. Ligand redistribution was not observed in this system.

(b) *Thiocyanate*. The reaction of an excess of AgNCS (or NH_4NCS) with $[NEt_4][PF_3Cl_3]$ gave a type of spectrum similar to that obtained with an excess of azide, *i.e.* a simple 1 : 3 : 3 : 1 quartet pattern [$\delta(^{31}P)$ − 185.6, $^1J_{PF}$ 732 Hz]. In this case, however, it appears from the shift value that the meridional isomer is formed (Table 1), and that *fac*-$[PF_3(NCS)_3]^-$ presumably is isomerised to the more stable form. This is perhaps not surprising in view of the conclusion that $[PCl_3(NCS)_3]^-$, formed by reaction of $[PCl_6]^-$ with NH_4NCS, exists exclusively as the *mer* isomer,[9] probably because of steric effects caused by the bulky NCS ligands.[21] If the configuration has been correctly assigned, this ion, too, must be fluxional at the n.m.r. operating temperature. The compound $[NEt_4][PF_3(NCS)_3]$ was isolated as an unstable yellow solid, which readily decomposed at or below room temperature. Its n.m.r. spectrum was identical with that just described.

In the presence of smaller quantities of AgNCS two distinct reactions were observed. Rapid replacement of Cl by NCS occurred initially, giving *fac*-$[PF_3Cl_2(NCS)]^-$ and *fac*-$[PF_3Cl(NCS)_2]^-$, the configurations of which were assigned by comparison of the experimental shifts with those calculated from pairwise additivity (Table 2). This was followed by ligand redistribution, giving rise to complex ^{31}P n.m.r. spectra. Resonances assignable to $[PF_5(NCS)]^-$, *cis*-$[PF_4(NCS)_2]^-$, [quintet, $\delta(^{31}P)$ −174.2, $^1J_{PF}$ 735 Hz], and *cis*-$[PF_2(NCS)_4]^-$ (Table 1) were observed. Exchange did not take place when $[PF_3(NCS)_3]^-$ was prepared using an excess of NCS^-, implying that the substitution reactions are faster than ligand exchange, which only occurs when two or more phosphorus(V) anions are present in solution.

The results show that *cis*-$[PF_4(NCS)_2]^-$ is also fluxional, if its configuration has been correctly deduced. A rather different chemical shift of δ −159.7 has been reported for non-fluxional *cis*-$[PF_4(NCS)_2]^-$ in MeCN solution at low temperature.[8] This value seems somewhat low (numerically) by comparison with the calculated shifts for both isomers, however. A quintet at δ −173.3, assigned to (fluxional) *cis*-$[PF_4(NCS)_2]^-$, was also detected in an exchange reaction between $[PF_6]^-$ and $[PF_3(NCS)_3]^-$ in the present work, together with signals from $[PF_5(NCS)]^-$ and the starting materials.

(3) *Substitution into* cis-$[PF_2Cl_4]^-$.—(a) *Azide.* The reaction between *cis*-$[PF_2Cl_4]^-$ and LiN_3 was carried out in the presence of an excess of $N(n\text{-}C_5H_{11})_4Cl$ to suppress any dissociation of anionic species. When an excess of LiN_3 was used, a triplet at -158.3, $^1J_{PF}$ 853 Hz, ascribed to *cis*-$[PF_2(N_3)_4]^-$, was observed in the ^{31}P n.m.r. spectrum. With smaller quantities of the azide, two further triplets were seen, as indicated in Table 3. The structural assignments are also shown, based on the splitting pattern and the calculated chemical shifts, since these ions are not expected to be fluxional. The replacement of each Cl by N_3 is expected to increase the susceptibility of the compound to further substitution, as observed in other azidochloro-systems,[11,22] so the failure to observe $[PF_2Cl(N_3)_3]^-$ could be due to its rapid reaction to form the fully substituted anion, keeping its concentration below the detection limit. Decomposition with loss of N_2 occurred even in the presence of an excess of halide. The ^{31}P n.m.r. spectrum after 2 days contained an intense doublet (δ -14.6, $^1J_{PF}$ 945 Hz), assigned to an NPClF or $NP(N_3)F$ unit in a polymeric phosphazene.

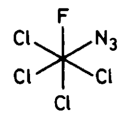
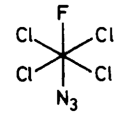
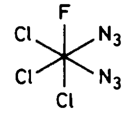
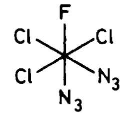
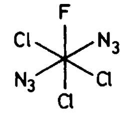
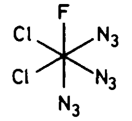
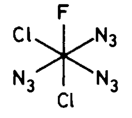
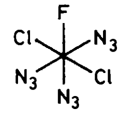
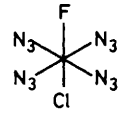
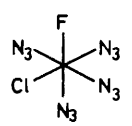
(b) *Thiocyanate.* The addition of a small quantity of AgNCS to *cis*-$[PF_2Cl_4]^-$ gave rise to two doublets of doublets and a triplet in the ^{31}P n.m.r. spectrum, ascribed to a series of substituted anions as shown in Table 3. The assignments are based on the splitting and calculated chemical shifts, and seem unambiguous. Substitution was rapid in this system, and neither of the possible isomers of *cis*-$[PF_2Cl_3(NCS)]^-$ was observed. The splitting patterns show clearly that these ions are not fluxional under the experimental conditions. The reaction was accompanied by decomposition, the products of which gave triplet resonances at δ -33.0 ($^1J_{PF}$ 1 001 Hz) and -15.6 ($^1J_{PF}$ 969 Hz). The nature of these species was not investigated further.

(4) *Substitution into* $[PFCl_5]^-$ *by Azide.*—The reaction of $[NEt_4][PFCl_5]$ [in $MeNO_2$ solution in the presence of $N(n\text{-}C_5H_{11})_4Cl$] with a large excess of LiN_3 produced a solution showing a doublet [$\delta(^{31}P)$ -168.3, $^1J_{PF}$ 870 Hz], readily ascribed to $[PF(N_3)_5]^-$. Smaller quantities of LiN_3 gave rise to a series of substituted anions, as shown in Table 4. The configurations indicated in Table 4 are based solely on the calculated shifts, as no structural information is available from the P–F splitting pattern in this case. Even so, configurations can be unambiguously assigned to the first two members of the series. The structure of $[PFCl_2(N_3)_3]^-$ cannot be deduced on this basis since the two plausible isomers have almost identical calculated shifts, very close to the observed value. The penultimate member of the series was again not observed, presumably because of rapid replacement of Cl by N_3. Decomposition was rapid in this system, giving rise to intense resonances to high frequency of the anion signals in the ^{31}P n.m.r. spectrum. No attempt was made to analyse this region of the spectrum in detail.

Insufficient starting material was available to investigate the reaction of $[PFCl_5]^-$ with thiocyanate. Attempts at direct substitution by N_3^- or NCS^- into PF_6^- were unsuccessful; the P–F bond is clearly resistant to substitution, although it takes part in ligand redistribution reactions.

From the foregoing results, the azido-complexes are evidently less labile than the corresponding thiocyanato-species; the reaction between $[PF_6]^-$ and $[P(N_3)_6]^-$ is slow, and $[PF_3Cl_{3-n}(N_3)_n]^-$ ions do not undergo ligand exchange. This behaviour could be related to the kinetic stability of $[P(N_3)_6]^-$ which is indefinitely stable in solution,[11,20,23] whereas $[P(NCS)_6]^-$ readily decomposes.[9]

Table 4. Calculated and observed chemical shifts (δ values) and coupling constants (Hz) for $[PFCl_{5-n}(N_3)_n]^-$ ($1 \leqslant n \leqslant 5$)

Ion	Structure	$\delta_{calc.}$	$\delta_{obs.}$	$^1J_{PF}$
$[PFCl_4(N_3)]^-$		-194.0	-193.9	998
		-176.8		
$[PFCl_3(N_3)_2]^-$		-174.5	-169.5	911
		-157.3		
		-157.2		
$[PFCl_2(N_3)_3]^-$		-155.1	-156.3	882
		-155.0		
		-137.8		
$[PFCl(N_3)_4]^-$		-152.8		
		-152.9		
$[PF(N_3)_5]^-$	One isomer		-168.3	870

The fluxional nature of some of these ions is also noteworthy, inasmuch as the more highly fluorinated ions $[PF_5(NCS)]^-$, *cis*-$[PF_4(NCS)_2]^-$, *mer*-$[PF_3(NCS)_3]^-$, and possibly *mer*-$[PF_3(N_3)_3]^-$ appear to be fluxional at the n.m.r. operating temperature. The $[PF_3Cl_{3-n}X_n]^-$ ($n = 0$, 1, or 2) ions are clearly non-fluxional at this temperature, as are the species with two (and presumably one) fluorines present. Variable temperature studies would provide a powerful method for the investigation of these systems in more detail, and might enable elucidation of the mechanism of fluxionality. Without such information a rationalisation of the above observations can only be tentative. If the transition state in the molecular rearrangement requires the participation of higher energy *d* orbitals on the phosphorus atom, however, electronegative substituents such as F or N_3 may well increase the availability of these orbitals and lower the energy barrier to the fluxional process.

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