Some Novel Phosphoranides containing Pentafluorophenyl Groups

Rusmidah Ali and Keith B. Dillon *
Chemistry Department, University of Durham, South Road, Durham DH1 3LE

Several novel phosphoranides containing pentafluorophenyl groups, of formulae $[P(C_6F_5)X_2Y]^-$ (X = Cl, Y = Cl, Br, or I; X = Br, Y = Br or I; X = NCS, Y = Cl, Br, I, or NCS) or $[P(C_6F_5)_2X(Y)]^-$ (X = Cl, Y = Cl, Br, or I; X = Br, Y = Br or I; X = CN, Y = Cl, Br, I, or NCS) have been identified in solution by means of ^{31}P n.m.r. spectroscopy. Most of the species have been isolated as salts with tetra-alkylammonium ions, and further characterised by elemental analysis and (in some cases) i.r. spectroscopy. These ions {apart from $[P(C_6F_5)_2(CN)Y]^-$} represent the first simple phosphoranides with an organo-group attached to phosphorus and no cyano-groups present. The species with two pentafluorophenyl groups are the first phosphoranides with two organo-groups directly bound to phosphorus. No acceptor properties towards halide ions were shown by $P(CCl_3)Cl_2$ or $P(C_6F_5)_2(NCS)$.

The first phosphoranide, or hypervalent anionic phosphorus(III) complex, PBr_4^-, was isolated (as its NPr_4^+ salt) in 1969,[1] and its crystal structure was later determined.[2] Several other ions of this type have subsequently been identified,[2–15] but until recently no phosphoranides with an organo-group R attached to phosphorus had been reported for simple non-cyclic systems.[10,14,16] In a very recent paper from this group, synthetic and spectroscopic studies on some phosphoranides $[PR(CN)_2X]^-$, where R = Me, Et, Ph, or C_6F_5 and X = Cl, Br, I, or NCS, including an *X*-ray crystal-structure determination for $[NEt_4][PPh(CN)_2Cl]$, have been described.[16] Even in these compounds, however, the presence of highly electronegative cyano-groups was necessary to achieve stability, presumably by helping to delocalise the formal negative charge on phosphorus. No acceptor properties towards halide ions were shown by $PMeCl_2$ or $PPhCl_2$,[17] with no cyano-groups, or by $PMe_2(CN)$ or $PPh_2(CN)$,[16] with two organic substituents on phosphorus.

In the present work we have extended the range of known phosphoranides by using electronegative pentafluorophenyl groups as the organic residues. By this means we have succeeded in preparing anions of formulae $[P(C_6F_5)X_2Y]^-$ (**1**) (X = Cl, Y = Cl, Br, or I; X = Br, Y = Br or I; X = NCS, Y = Cl, Br, I, or NCS) and $[P(C_6F_5)_2X(Y)]^-$ (**2**) (X = Cl, Y = Cl, Br, or I; X = Br, Y = Br or I). These are the first simple phosphoranides with an organo-group on phosphorus and no CN groups present. We have also synthesised the derivatives $[P(C_6F_5)_2(CN)Y]^-$ (**3**) (Y = Cl, Br, I, or NCS). The species of types (**2**) and (**3**) are the first such ions with two R groups on phosphorus. Some of the new complexes were unstable to isolation, although all could be recognised in solution by their characteristic lower frequency (upfield) shift relative to the precursor phosphine.[10,16] Most species, however, have been isolated as their tetra-n-alkylammonium salts, and further characterised by elemental analysis and (in some cases) i.r. spectroscopy. No acceptor properties towards halide ions were shown by $P(CCl_3)Cl_2$, with an alternative electronegative organic substituent on phosphorus, or by $P(C_6F_5)_2(NCS)$. A preliminary account of this work was presented at the 10th International Conference on Phosphorus Chemistry in Bonn.[14]

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 salts, which were dried as described previously.[18]

(*a*) *Preparation of the Precursor Phosphines.*—The syntheses of $P(C_6F_5)Cl_2$, $P(C_6F_5)Br_2$, and $P(C_6F_5)(NCS)_2$ have been described in earlier publications.[16,19] The compound $P(C_6F_5)_2Br$ was prepared by the reaction of $Mg(C_6F_5)Br$ with PBr_3 in a 2:1 molar ratio; it was isolated as a colourless liquid boiling between 385 and 387 K at 0.5 mmHg (*ca.* 67 Pa) [$\delta(^{31}P)$ 11.4 p.p.m. (CH_2Cl_2); lit.,[20] 13.0 p.p.m. (neat liquid)]. The compound $P(C_6F_5)_2Cl$ was obtained by exchange between $P(C_6F_5)_2Br$ and a slight excess of NEt_4Cl, similar to the synthesis of $P(C_6F_5)Cl_2$ from $P(C_6F_5)Br_2$.[19] Phosphorus-31 n.m.r. spectroscopy was used to verify that the reaction had gone to completion, and the product was isolated as a colourless liquid [$\delta(^{31}P)$ 37.1 p.p.m. (hexane or CH_2Cl_2); lit.,[20] 37 p.p.m. (neat liquid)]. The compound $P(C_6F_5)_2(CN)$ was prepared by addition of an equimolar amount of AgCN to a solution of $P(C_6F_5)_2Cl$ in CH_2Cl_2, with constant stirring, which was continued for 1 h. The silver salts were filtered off, the solvent was removed *in vacuo*, and the product was isolated as a cream-coloured solid after scratching the flask containing the residual liquid with a spatula [$\delta(^{31}P)$ −93.5 p.p.m. in CH_2Cl_2 or $PhNO_2$; lit.,[21] −100.2 p.p.m. in C_6H_6 or $CHCl_3$]. The compound $P(C_6F_5)_2(NCS)$ was similarly obtained by stirring $P(C_6F_5)_2Br$ with excess of AgSCN for 2—3 h. A yellow liquid was isolated after removal of silver salts and CH_2Cl_2 [$\delta(^{31}P)$ 9.8 p.p.m.; lit.,[21] 12.4 p.p.m. in C_6H_6 or $CHCl_3$]. The compound $P(CCl_3)Cl_2$ was prepared by a modification of the method of Quin and Rolston.[22] Tetrachloromethylphosphane, obtained by chlorination of $PMeCl_2$, was added to either CH_2Cl_2 or CCl_4, and the mixture was warmed to 343—353 K until all of the solid had dissolved. Excess of dry Cl_2 gas was allowed to flow in at a slow rate until a greenish yellow solution formed. The solvent and excess of Cl_2 were removed *in vacuo*, and the product $P(CCl_3)Cl_4$ was isolated as a fine white solid. This compound was then dissolved in CH_2Cl_2 and warmed to 308 K on a water-bath. An equimolar quantity of $P(OMe)Cl_2$, prepared by the reaction of PCl_3 with MeOH,[23] was added, with constant stirring. After 30 min the solvent and volatiles were removed *in vacuo* to leave $P(CCl_3)Cl_2$ as a white solid [$\delta(^{31}P)$ 149.6 p.p.m. (CH_2Cl_2); lit.,[24] 148.6 p.p.m. (CCl_4)].

Table 1. Elemental analyses (%) of new phosphorus compounds

	Found				Calc.			
Compound	C	P	X[a]	Y[b]	C	P	X[a]	Y[b]
$[NPr_4][P(C_6F_5)Cl_2I]$	39.5	4.7	11.5	22.2	37.1	5.3	12.2	21.8
$[NEt_4][P(C_6F_5)(NCS)_2Cl]$	41.7	6.0	12.0	7.1	40.0	6.5	13.4	7.4
$[NPr_4][P(C_6F_5)(NCS)_2Cl]$	45.0	5.8	11.3	6.6	44.8	5.8	12.0	6.6
$[NPr_4][P(C_6F_5)(NCS)_2Br]$	40.4	4.5	9.5	16.6	41.4	5.3	11.0	13.8
$[NPr_4][P(C_6F_5)(NCS)_2I]$	37.6	5.3	10.2	21.0	38.3	4.9	10.2	20.2
$[NEt_4][P(C_6F_5)(NCS)_3]$	41.6	6.3	19.6	—	40.6	6.2	19.1	—
$[NEt_4][P(C_6F_5)_2Cl_2]$	43.0	5.2	11.5	—	42.4	5.5	12.5	—
$[NPr_4][P(C_6F_5)_2Cl_2]$	44.2	4.4	10.2	—	46.3	5.0	11.4	—
$[NPr_4][P(C_6F_5)_2Cl(Br)]$	44.2	4.5	*c*	*c*	43.2	4.7	5.3	12.0
$[NPr_4][P(C_6F_5)_2Cl(I)]$	40.9	4.1	5.2	21.4	40.4	4.3	5.0	17.8
$[NPr_4][P(C_6F_5)_2Br_2]$	40.4	3.8	24.9	—	40.5	4.4	22.5	—
$[NPr_4][P(C_6F_5)_2Br(I)]$	36.5	3.9	11.8	17.5	38.0	4.1	10.5	16.7
$[NEt_4][P(C_6F_5)_2(CN)Cl]$	47.0	4.8	7.8	—	45.3	5.6	6.4	—
$[NPr_4][P(C_6F_5)_2(CN)Br]$	49.8	4.2	12.3	—	45.7	4.7	12.2	—
$[NPr_4][P(C_6F_5)_2(CN)I]$	41.4	4.3	17.9	—	42.6	4.4	18.0	—
$[NEt_4][P(C_6F_5)_2(CN)(NCS)]$	44.6	5.6	*d*	—	45.6	5.4	5.5	—

[a] X = Cl, S, or Br. [b] Y = I, Cl, or Br (whichever comes first in the formula is taken as X). [c] See text. [d] Not determined.

(*b*) *N.M.R. and Synthetic Studies of the Phosphoranides.*—As in earlier work,[16] an excess of the anion Y^-, in the form of a solution of one of its tetra-alkylammonium salts, was initially added to a solution of the precursor phosphine in an inert organic solvent (usually CH_2Cl_2), until the maximum low-frequency (upfield) shift [10,16] of the ^{31}P resonance was obtained. This limiting shift in some instances depended markedly on the cation (Results and Discussion). Formation of phosphoranides was established for $P(C_6F_5)Cl_2$ with Cl^-, Br^-, and I^- ions, for $P(C_6F_5)Br_2$ with Br^- and I^-, for $P(C_6F_5)(NCS)_2$ with Cl^-, Br^-, I^-, and NCS^-, for $P(C_6F_5)_2Cl$ with Cl^-, Br^-, and I^-, for $P(C_6F_5)_2Br$ with Br^- or I^-, and for $P(C_6F_5)_2(CN)$ with Cl^-, Br^-, I^-, and NCS^-. No complex formation between $P(C_6F_5)_2(NCS)$ or $P(CCl_3)Cl_2$ and halide ions was observed, the ^{31}P resonances remaining unchanged (within experimental error) on addition of tetra-alkylammonium salts. For the systems where phosphoranides were formed, the experiments were repeated with a 1:1 molar ratio of the reactants, and attempts were made to isolate the products by removal of the solvent *in vacuo*. It proved to be impossible under our experimental conditions to isolate compounds containing the ions $[P(C_6F_5)Cl_3]^-$, $[P(C_6F_5)Cl_2Br]^-$, $[P(C_6F_5)Br_3]^-$, and $[P(C_6F_5)Br_2I]^-$ in a pure state, since rapid decomposition of these species was observed. Rather surprisingly, perhaps, the phosphoranides containing two C_6F_5 groups were more stable, even with halides as the only other ligands, and salts containing these ions, as well as all the other species mentioned above, were successfully isolated. Elemental analyses (C, P, X, and Y) for new compounds, obtained as in earlier work,[25,26] are given in Table 1. Many of the products were very unstable, and as a consequence these analyses are often not of the standard expected for stable materials, although they were obtained as rapidly as possible after isolation of the compound. The procedure adopted was to have the preweighed capsule for combustion of the sample ready in a glove-box, so that it could be filled as soon as the compound had been isolated, but some discrepancies are still apparent. Despite these limitations, all carbon analyses but one in Table 1 are within ±6% of the theoretical figure, and all but three are within ±4%. Phosphorus analyses are rather low in most cases, with just one more than 4% above the expected value. These results nevertheless show clearly that starting materials have not been isolated, and that the phosphoranides have indeed been formed. Phosphorus-31 n.m.r. spectra were recorded on a Fourier-transform spectrometer at 307.2 K, as described previously;[18] chemical shifts are expressed relative to 85% H_3PO_4, with the higher-frequency (downfield) direction taken as positive. I.r. spectra were obtained as in previous work.[25]

Results and Discussion

(*a*) *Complex Formation by* $P(C_6F_5)X_2$ ($X = Cl$, Br, or NCS).—When NR_4Cl was added to a solution of $P(C_6F_5)Cl_2$ in CH_2Cl_2 the ^{31}P resonance, initially at 135.6 p.p.m. (lit., 137.0,[20] 136.7 p.p.m.[27]), moved upfield. The limiting shift depended quite markedly on R, the values being 109.3, 100.0, and 96.5 p.p.m. for R = Et, Pr^n, and $n\text{-}C_5H_{11}$ respectively. Similar variations of limiting shift with cation were also observed for some of the phosphoranides $[PR(CN)_2X]^-$.[16] The reason for this behaviour is not clear, although there could be a contribution to shielding of phosphorus by the bulkier cation, if the compound exists in CH_2Cl_2 as an ion pair. (For phosphoranides which are stable in solution, any movement in the shift tends to be to lower frequency with increasing cation size.) Attempts to isolate the adduct from 1:1 reactions between $P(C_6F_5)Cl_2$ and NEt_4Cl or $NPr^n{}_4Cl$ led to mixtures containing (from the elemental analysis) some $NR^n{}_4Cl$ as well as the phosphoranide, and a pure product could not be obtained. Similar behaviour was observed when $NPr^n{}_4Br$ was added to a solution of $P(C_6F_5)Cl_2$; the limiting shift was established as 124.2 p.p.m., but a pure solid could not be isolated from a 1:1 reaction. With $NPr^n{}_4I$, however, the limiting shift was found to be 132.2 p.p.m., and the solid from the 1:1 reaction analysed as the adduct (Table 1). It redissolved in $PhNO_2$ to give a signal at 131.9 p.p.m. The limiting shifts for all the $P(C_6F_5)X_2$ adducts studied are listed in Table 2. It was not possible to form a phosphoranide by addition of NEt_4NCS to a solution of $P(C_6F_5)Cl_2$, since substitution occurred in preference to addition.

Similarly, complex formation between $P(C_6F_5)Br_2$ and NR_4Cl could not be studied, since substitution occurred. [This reaction has been used to prepare $P(C_6F_5)Cl_2$ from $P(C_6F_5)Br_2$.[19]] On addition of $NPr^n{}_4Br$ to a solution of $P(C_6F_5)Br_2$ in CH_2Cl_2, the resonance, initially at 111.3 p.p.m. (lit.,[20] 113.5 p.p.m.) moved to 98.3 p.p.m. A similar limiting shift of 99.7 p.p.m. was obtained by using $N(n\text{-}C_6H_{13})_4Br$. A pure phosphoranide could not be isolated from a 1:1 reaction, however, and from analysis the product appeared to consist of a mixture

Table 2. Values of $\delta(^{31}P)$ (p.p.m.) for $P(C_6F_5)X_2$ and $[NR_4][P(C_6F_5)X_2Y]$ in CH_2Cl_2 solution

Compound	$\delta(^{31}P)$	Compound	$\delta(^{31}P)$
$P(C_6F_5)Cl_2$	135.6	$[N(n\text{-}C_6H_{13})_4][P(C_6F_5)Br_3]$	99.7
$[NEt_4][P(C_6F_5)Cl_3]$	109.3	$[NPr^n{}_4][P(C_6F_5)Br_2I]$	90.0
$[NPr^n{}_4][P(C_6F_5)Cl_3]$	100.0	$P(C_6F_5)(NCS)_2$	61.2
$[N(n\text{-}C_5H_{11})_4][P(C_6F_5)Cl_3]$	96.5	$[NEt_4][P(C_6F_5)(NCS)_2Cl]$	32.5
$[NPr^n{}_4][P(C_6F_5)Cl_2Br]$	124.2	$[NPr^n{}_4][P(C_6F_5)(NCS)_2Br]$	37.1
$[NPr^n{}_4][P(C_6F_5)Cl_2I]$	132.2	$[NPr^n{}_4][P(C_6F_5)(NCS)_2I]$	58.0
$P(C_6F_5)Br_2$	111.3	$[NEt_4][P(C_6F_5)(NCS)_3]$	51.6
$[NPr^n{}_4][P(C_6F_5)Br_3]$	98.3		

of the adduct and $NPr^n{}_4Br$. The results for addition of I^- ions, discussed below, strongly suggest that formation of the anion $[P(C_6F_5)Br_3]^-$ is incomplete even in the presence of excess of Br^- ions, although there is clear evidence for its partial formation in solution; the single peak observed would then represent a rapidly exchanging system between $P(C_6F_5)Br_2$ and $[P(C_6F_5)Br_3]^-$.

Addition of NPr_4I to a solution of $P(C_6F_5)Br_2$ gave a limiting shift of 90.0 p.p.m. The product isolated from a 1:1 molar ratio reaction gave a low bromine analysis, and appeared not to be the pure phosphoranide. In all other systems, both in this work and in those described previously,[16] the shift to lower frequency on phosphoranide formation is larger for addition of Br^- ions to a phosphine than for addition of I^- ions. Hence partial formation only of $[P(C_6F_5)Br_3]^-$ may reasonably be inferred, and it is also not possible to assert with certainty that complete formation of $[P(C_6F_5)Br_2I]^-$ has been observed. Nevertheless there seems no doubt that these ions do exist in solution, even if only as components of rapidly exchanging systems.

The thiocyanatophosphine $P(C_6F_5)(NCS)_2$ formed phosphoranides with each of Cl^-, Br^-, I^-, and NCS^-; the limiting shifts obtained are included in Table 2. The shifts follow the sequence observed for the $[PR(CN)_2X]^-$ ions,[16] with Cl^- giving the largest shift to lower frequency, and $Cl^- > Br^- > NCS^- > I^-$. The complexes were successfully isolated from 1:1 reactions in all cases; the compounds were either coloured sticky solids (NEt_4Cl, orange; NEt_4NCS, red) or viscous liquids ($NPr^n{}_4Cl$, brown; $NPr^n{}_4Br$, yellow), except for the adduct with $NPr^n{}_4I$, which was a yellow solid. They all tended to darken or go red on standing, even in the refrigerator or at room temperature in a glove-box. When the compounds were redissolved immediately after isolation they gave shifts intermediate between those of $P(C_6F_5)(NCS)_2$ and $[P(C_6F_5)(NCS)_2Y]^-$, showing that some dissociation occurs in solution. The compound $[NPr^n{}_4][P(C_6F_5)(NCS)_2Cl]$, for example, gave a signal at 48.4 p.p.m. when redissolved in $PhNO_2$. The i.r. spectra of the adducts with $NPr^n{}_4Cl$ and $NPr^n{}_4Br$ were recorded in CH_2Cl_2 solution, and those with $NPr^n{}_4I$ and NEt_4NCS as Nujol mulls. All showed a strong, broad NCS band with two maxima between 2 025 and 1 940 cm^{-1}, differing from that for $P(C_6F_5)(NCS)_2$,[28] and indicating that the thiocyanato-groups are N-bonded in each case.[28–30] These are the first phosphoranides to be prepared from an organothiocyanatophosphine.

(*b*) *Complex formation by* $P(C_6F_5)_2X$ (X = Cl, Br, *or* CN).—Addition of a solution of NR_4Cl to a solution of $P(C_6F_5)_2Cl$ in CH_2Cl_2 caused a large shift of the signal to lower frequency; the limiting shifts were established as -24.2 p.p.m. for R = Et, -25.6 p.p.m. for R = Pr^n, and -41.8 p.p.m. for R = $n\text{-}C_5H_{11}$. The adducts were isolated from 1:1 reactions between $P(C_6F_5)_2Cl$ and NEt_4Cl or $NPr^n{}_4Cl$; the solid products gave signals at -19.5 and -11.4 p.p.m. respectively when redissolved in $PhNO_2$, showing that some dissociation occurs in this solvent. Limiting shifts of -6.3 p.p.m. for R = Pr^n and -27.0 p.p.m. for R = $n\text{-}C_6H_{13}$ were similarly obtained when NR_4Br was added to $P(C_6F_5)_2Cl$ (Table 3). The phosphoranide was isolated from a 1:1 reaction with $NPr^n{}_4Br$, but problems were encountered in the halogen analysis. The chlorine and bromine could not be determined separately, although qualitative tests confirmed that both were present. A total halide analysis gave 96.2% of the theoretical value, confirming that the adduct had been prepared. Tetra-n-propylammonium iodide gave a limiting shift of 29.5 p.p.m., and the phosphoranide was isolated from a 1:1 reaction. The lower-frequency shifts on addition of halide ion to $P(C_6F_5)_2Cl$ follow the expected order Cl > Br > I.[16] It is clear from the results for the chloride and bromide that the limiting shift is highly cation dependent in these systems, as in the $P(C_6F_5)Cl_2$–Cl^- system discussed previously.

Phosphoranide formation by $P(C_6F_5)_2Br$, as in the case of $P(C_6F_5)Br_2$, could only be investigated for addition of Br^- and I^- ions. The limiting shifts obtained are given in Table 3, with those for other $P(C_6F_5)_2X$ derivatives. The adducts were isolated as a yellow viscous liquid and a red solid from 1:1 reactions with $NPr^n{}_4Br$ and $NPr^n{}_4I$ respectively, and both were rather unstable.

Somewhat more stable phosphoranides containing two pentafluorophenyl groups were obtained from $P(C_6F_5)_2(CN)$, where the complexes $[P(C_6F_5)_2(CN)Y]^-$ were synthesised for Y = Cl, Br, I, or NCS. The limiting shifts are given in Table 3. The value for $[NR_4][P(C_6F_5)_2(CN)Cl]$ did not appear to be cation dependent with R = Et or Pr^n, since identical results were obtained within experimental error. The shifts relative to the precursor phosphine follow the sequence observed for the phosphoranides $[PR(CN)_2X]^-$ of Cl > Br > NCS > I,[16] *i.e.* the largest shift to lower frequency is caused by addition of chloride ions. All of the products were isolated from 1:1 reactions (Table 1). It proved impossible to obtain i.r. spectra from the adducts with Cl^- or Br^- since the compounds would not mull properly, and partially dissociated in solution. The compound $[NPr^n{}_4][P(C_6F_5)_2(CN)I]$ gave a medium-intensity CN band at 2 180 cm^{-1}, similar in frequency but stronger than the absorption from the parent phosphine,[28] while the thiocyanato-derivative $[NEt_4][P(C_6F_5)_2(CN)(NCS)]$ gave a strong, broad NCS band with maximum at 2 030 cm^{-1}, strongly suggesting that the NCS group is N- rather than S-bonded.[28–30] The CN stretching band of this compound was obscured by the broad NCS absorption.

(*c*) *General Discussion.*—The results described above have shown that phosphoranides containing one or two pentafluorophenyl groups may be prepared in solution, even without the presence of cyanide groups on phosphorus, and that several of the products may be isolated. These compounds are less stable than the derivatives $[NR_4][PR'(CN)_2X]$ described previously,[16] readily undergoing decomposition and/or hydrolysis. The complexes tend to be partially dissociated in solution, and an excess of the donor ion has to be used to establish the limiting shift value.

Table 3. Values of $\delta(^{31}P)$ (p.p.m.) for $P(C_6F_5)_2X$ and $[NR_4][P(C_6F_5)_2X(Y)]$ in CH_2Cl_2 solution

Compound	$\delta(^{31}P)$	Compound	$\delta(^{31}P)$
$P(C_6F_5)_2Cl$	37.1	$[NPr^n_4][P(C_6F_5)_2Br_2]$	−30.7
$[NEt_4][P(C_6F_5)_2Cl_2]$	−24.2	$[NPr^n_4][P(C_6F_5)_2Br(I)]$	−16.2
$[NPr^n_4][P(C_6F_5)_2Cl_2]$	−25.6	$P(C_6F_5)_2(CN)$	−93.5
$[N(n\text{-}C_5H_{11})_4][P(C_6F_5)_2Cl_2]$	−41.8	$[NEt_4][P(C_6F_5)_2(CN)Cl]$	−112.9
$[NPr^n_4][P(C_6F_5)_2Cl(Br)]$	−6.3	$[NPr^n_4][P(C_6F_5)_2(CN)Cl]$	−112.9
$[N(n\text{-}C_6H_{13})_4][P(C_6F_5)_2Cl(Br)]$	−27.0	$[NPr^n_4][P(C_6F_5)_2(CN)Br]$	−101.6
$[NPr^n_4][P(C_6F_5)_2Cl(I)]$	29.5	$[NPr^n_4][P(C_6F_5)_2(CN)I]$	−95.1
$P(C_6F_5)_2Br$	11.4	$[NPr^n_4][P(C_6F_5)_2(CN)(NCS)]$	−98.4

It was not possible to obtain thiocyanato-adducts from $P(C_6F_5)X_2$ or $P(C_6F_5)_2X$ where X = halogen, since substitution occurred in preference to addition. Similarly, chloro-derivatives could not be obtained from treating $P(C_6F_5)Br_2$ or $P(C_6F_5)_2Br$ with NR_4Cl, since substitution again took place, *although* the phosphoranide $[P(C_6F_5)_2Cl(Br)]^-$ could be prepared by using $P(C_6F_5)_2Cl$ as the starting phosphine. Where complete or partial series of adducts were observed, the shifts followed the same sequence as that reported[16] for $[PR(CN)_2X]^-$, with Cl > Br > NCS > I, except for the $P(C_6F_5)Br_2$ adducts with Br^- and I^- ions, where a larger shift to lower frequency was found on formation of the iodo-derivative. This result suggests that the limiting shift for $[P(C_6F_5)Br_3]^-$ may well not have been reached, and that this phosphoranide is only partially formed, even in the presence of a large excess of bromide ions.

The results described above provide further support for the participation of phosphoranides as unstable intermediates in nucleophilic substitution reactions of anions at organophosphorus(III) centres, since phosphoranides have now been obtained with one or two organo-groups on phosphorus, even without the presence of stabilising cyano-groups. Clearly the organic substituents have to be highly electronegative for such derivatives to be isolable, presumably because they then assist in the delocalisation of the formal negative charge on phosphorus. This is confirmed by the failure to observe phosphoranide formation under our experimental conditions by addition of halide ions to $PRCl_2$ [R = Me,[17] CCl_3 (this work), or Ph[17]], $PR_2(CN)$ (R = Me or Ph),[16] or $P(C_6F_5)_2(NCS)$ (this work). Nevertheless the occurrence of such species as unstable intermediates, even for organophosphorus(III) compounds with less electronegative groups on phosphorus, appears to be a very reasonable postulate in a nucleophilic substitution reaction. At the very least, the range of known simple phosphoranides has been considerably extended by the present work.

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