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FULL PAPER

The synthesis and characterisation of R_3PXCN [R = 2,4,6-$(CH_3O)_3C_6H_2$, 2,6-$(CH_3O)_2C_6H_3$, $NCCH_2CH_2$, C_6H_{11} or $PhCH_2$; X = Br or I] in the solid state and in solution

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The compounds R_3PXCN [R = 2,4,6-$(CH_3O)_3C_6H_2$, 2,6-$(CH_3O)_2C_6H_3$, $NCCH_2CH_2$, C_6H_{11} or $PhCH_2$; X = Br or I] have been synthesized and characterised by elemental analysis, X-ray powder diffraction and infrared and ^{31}P-{H} NMR spectroscopy. In the solid state and in solution the compounds exist as mixtures of the ionic compounds $[R_3PCN]X$ and $[R_3PX]CN$ with no evidence for the species R_3PX_2 or $R_3P(CN)_2$. Infrared studies indicate the presence of both covalently bound and ionic cyanide. The ^{31}P-{H} NMR studies show that in $CDCl_3$ the compounds exist predominantly as $[R_3PCN]X$, although a minor component due to $[R_3PX]CN$ is also observed in *ca.* 10:1 ratios. These novel compounds are discussed with reference to the analogous R_3PX_2 compounds. An X-ray crystallographic study of $[\{2,4,6\text{-}(CH_3O)_3C_6H_2\}_3PCN]I$ reveals an ionic structure with no long cation–anion interactions. In contrast, the crystal structure of $[2,4,6\text{-}(CH_3O)_3C_6H_2]_3PI_2$ represents a further example of the molecular four-co-ordinate charge-transfer structure R_3P–I–I; *d*(I–I) for this compound, 3.3394(5) Å, is rather short considering the very high basicity of the parent tertiary phosphine [*cf. d*(I–I) for $PhMe_2PI_2$ = 3.408(5) Å].

The nature of compounds formed from the reaction of tertiary phosphines and dihalogens is of considerable current interest.[1–6] The principal reason for this is the surprisingly complex and varied solid-state structural chemistry associated with compounds of stoichiometry R_3PX_2. It has been established that such compounds lie close to the structural (ionic/molecular) borderline, the nature of R and X playing a crucial role in determining the structural nature, and, in some cases, the geometry of the phosphorus atom in the compound formed. For example, Ph_3PX_2 (X = Br[3] or I[1]) prepared from diethyl ether solution exhibits a molecular four-co-ordinate charge-transfer structure, Ph_3PX–X, whereas the analogous dichlorine compound adopts a trigonal bipyramidal structure[7] when prepared in the same solvent. When a more basic tertiary phosphine is employed both the dibromine compound $[Et_3PBr]Br$[3] and the dichlorine compound $[Pr^n{}_3PCl]Cl$[6] are ionic in the solid state and contain long cation–anion interactions as well as interactions between the X^- anion and the δ^+ hydrogens on the aliphatic groups of the tertiary phosphine. In contrast, a crystallographic study of a diiodo compound containing a basic tertiary phosphine, $PhMe_2PI_2$,[1] revealed that this compound favours the charge-transfer species, $PhMe_2PI$–I [*d*(I–I) = 3.408(5) Å, the sum of the van der Waals radii for two iodine atoms = 4.3 Å].

Additionally, the nature of the solvent of preparation is important in the structure adopted for certain R_3PX_2 compounds. As previously mentioned, Ph_3PCl_2, prepared from the stoichiometric reaction of PPh_3 and Cl_2 in diethyl ether solution is trigonal bipyramidal.[7] However, if dichloromethane is used as solvent instead of diethyl ether then the solvated ionic dinuclear compound $[Ph_3PCl\cdots Cl\cdots ClPPh_3]Cl\cdot 2CH_2Cl_2$ is isolated in quantitative yield,[6] with no trigonal bipyramidal product being observed. Clearly, Ph_3PCl_2 lies very close to the ionic/molecular structural borderline, the relative permittivity (polarity) of the solvent determining the nature of the product formed.

Related studies concerning the reactions of interhalogens, IX (X = Br or Cl), with tertiary phosphines have also been reported. An X-ray crystallographic study[8] of the product formed from the reaction of Ph_3P and IBr in diethyl ether solution revealed a molecular charge-transfer species of composition $Ph_3PI_{1.29}Br_{0.71}$; the halogen sites of the compound being of dual occupancy, and the compound as a whole being rich in iodine with respect to bromine. Nevertheless, the compound exists predominantly as Ph_3P–I–Br, *i.e.* with the heavier halogen bound directly to the phosphorus atom.[8] There is evidence that the structure of Ph_3PIBr is also solvent dependent; a solution ^{31}P-{H} NMR study[9] of this compound in $CDCl_3$ revealed a single peak at δ 44.2, identical to that observed for $[Ph_3PI]I$. In contrast, if Ph_3PIBr is dissolved in CD_3CN solution, a single peak at δ 51.7 is observed, identical to that observed for $[Ph_3PBr]Br$. It therefore seems certain that in $CDCl_3$ Ph_3PIBr exists as $[Ph_3PI]Br$, whereas in CD_3CN solution it exists as $[Ph_3PBr]I$. This phenomenon was rationalised to be due to the susceptibility of the P–I bond to attack by the Br anion in highly polar solvents.[9]

Despite the current interest in the nature of compounds formed between triorganophosphorus species and dihalogens or interhalogens, reports of such compounds concerning mixed halogen/pseudohalogens are non-existent. We therefore decided to investigate the nature of compounds of stoichiometry R_3PXCN (X = Br or I) because, firstly, nothing is known about their structures and, secondly, we were intrigued to know if the compounds would adopt the charge-transfer structure, a trigonal bipyramidal structure or the ionic structures $[R_3PCN]X$ or $[R_3PX]CN$. Additionally, if an ionic structure was to be adopted by these compounds, it would also be interesting to establish whether the halogen atom or the cyanide moiety would bind directly to the phosphorus atom.

Results and Discussion

The R_3PXCN compounds prepared in this study were synthesised by the direct reaction of stoichiometric quantities of the tertiary phosphine and XCN in diethyl ether solution at room temperature (r.t.), equation (1). The compounds were

$$R_3P + XCN \xrightarrow[\text{3 d, r.t.}]{\text{Et}_2\text{O, N}_2} R_3PXCN \qquad (1)$$

prepared in essentially quantitative yield; analytical data are presented in Table 1. The compounds had a tendency to be rich in halogen and deficient in nitrogen; however, after several repeat syntheses and subsequent analyses, satisfactory elem-

Table 1 Analytical data for R_3PXCN[a]

Compound	Colour	C	H	N	X[b]
$[2,4,6\text{-}(CH_3O)_3C_6H_2]_3PICN$	Yellow	48.4 (49.1)	5.0 (4.8)	1.7 (2.0)	18.9 (18.5)
$[2,6\text{-}(CH_3O)_2C_6H_3]_3PICN$	Yellow	49.2 (50.4)	4.6 (4.5)	2.0 (2.4)	22.7 (21.3)
$(NCCH_2CH_2)_3PICN$	Brown	33.3 (34.7)	4.1 (3.5)	14.0 (16.2)	38.4 (36.7)
$(C_6H_{11})_3PICN$	Buff	51.1 (52.7)	7.6 (7.6)	2.8 (3.2)	29.9 (29.3)
$(PhCH_2)_3PICN$	Cream	57.7 (57.8)	4.8 (4.6)	2.1 (3.1)	27.4 (27.8)
$[2,4,6\text{-}(CH_3O)_3C_6H_2]_3PBrCN$	Beige	52.8 (52.7)	5.5 (5.2)	1.9 (2.2)	12.1 (12.5)
$[2,6\text{-}(CH_3O)_2C_6H_3]_3PBrCN$	White	54.1 (54.7)	5.0 (4.9)	2.0 (2.6)	15.6 (14.6)
$(NCCH_2CH_2)_3PBrCN$	White	39.9 (40.1)	4.7 (4.0)	17.9 (18.7)	26.9 (26.8)
$(C_6H_{11})_3PBrCN$	White	58.6 (59.1)	8.6 (8.5)	2.5 (3.6)	21.7 (20.7)
$(PhCH_2)_3PBrCN$	White	63.9 (64.4)	5.8 (5.1)	1.9 (3.4)	20.3 (19.5)

[a] Calculated values in parentheses. [b] X = Br or I.

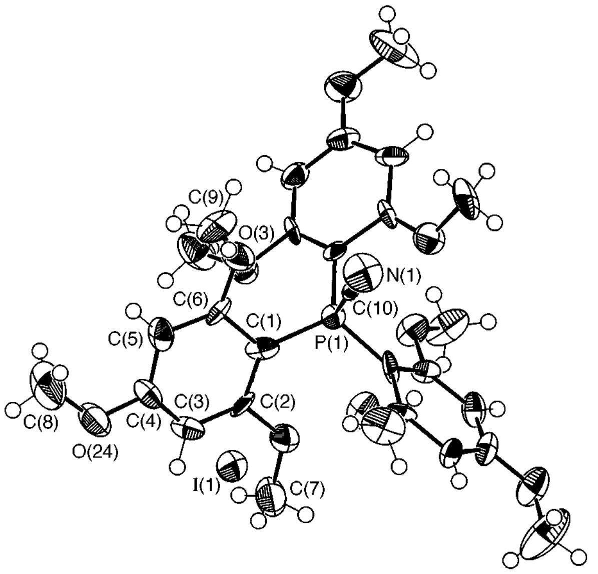

Fig. 1 The crystal structure of ionic $[\{2,4,6\text{-}(CH_3O)_3C_6H_2\}_3PCN]I$

Table 2 Selected bond lengths (Å) and angles (°) in $[\{2,4,6\text{-}(CH_3O)_3C_6H_2\}_3PCN]I$

N(1)–C(10)	1.19(5)
P(1)–C(1)	1.78(2)
C(1)–P(1)–C(1)	114.8(7)
C(1)–P(1)–C(10)	103.4(9)
C(2)–C(1)–P(1)	131(2)
C(6)–C(1)–P(1)	112(2)
N(1)–C(10)–P(1)	180.0

ental analysis data were eventually obtained. In the case of the reaction of $[2,4,6\text{-}(CH_3O)_3C_6H_2]_3P$ with ICN, recrystallisation of the pale yellow solid from dichloromethane solution at *ca.* 50 °C produced a large quantity of pale yellow crystals on standing at room temperature for *ca.* 3 d. The structure of the compound is revealed to be ionic, $[\{2,4,6\text{-}(CH_3O)_3C_6H_2\}_3PCN]I$, Fig. 1. Selected bond lengths and angles are displayed in Table 2. The structure is interesting for several reasons: firstly, that an ionic structure rather than a molecular trigonal bipyramidal one is revealed. Additionally, unlike the ionic compounds $[R_3PCl]Cl$ ($R = Pr^n$ or Pr^i)[4,6] and $[Et_3PBr]Br$,[3] which contain long cation–anion interactions, no interaction between the cation and anion in $[\{2,4,6\text{-}(CH_3O)_3C_6H_2\}_3PCN]I$ is noted; secondly, and more importantly, the pseudohalogen, CN, is bound directly to the phosphorus atom and not the iodine atom. This compound was prepared from diethyl ether solution. The susceptibility of a P–I bond to nucleophilic attack by an X^- anion in ionising solvents has previously been described,[9] producing $[R_3P\text{–}X]I$ (X = Br or Cl). However, in solvents of low polarity (such as diethyl ether) we have previously shown that for a series of compounds the compound containing the heavier halogen bound to the phosphorus atom, R_3PIBr, persists in both the solid state and in solution. Since $[\{2,4,6\text{-}(CH_3O)_3C_6H_2\}_3PCN]I$ was prepared from diethyl ether solution, it might have been expected that the iodine atom would bond directly to the phosphorus and an ionic cyanide ion would be exhibited. The reason why the cyanide binds to the phosphorus is not known with certainty but may be related to the fact that the parent tertiary phosphine is very basic. From the infrared spectrum of this material, two bands are observed, one attributable to ionic cyanide, CN^-, and the other to covalent cyanide (see infrared spectroscopic studies section). The latter band is the more intense and also the one which corresponds to the crystal structure. Nevertheless, the information gained from infrared studies suggests that the product $[\{2,4,6\text{-}(CH_3O)_3C_6H_2\}_3PI]CN$ may be present in the bulk material. Attempts to obtain single crystals of this material failed however, the only material isolated being $[\{2,4,6\text{-}CH_3O)_3C_6H_2\}_3PCN]I$, corresponding to the crystal structure reported, and in accord with solution $^{31}P\text{-}\{H\}$ NMR studies in $CDCl_3$.

The carbon–nitrogen distance in $[\{2,4,6\text{-}(CH_3O)_3C_6H_2\}_3PCN]I$, 1.19(5) Å, is comparable to the cyanide ion, 1.16(2) Å.[10] Although there are no previous examples of compounds of formula $[R_3PCN]X$, there a few reported species containing PCN bonds, *e.g.* the five-co-ordinated phosphirene[11] 1-(tetrachlorocatecholato-*O*,*O′*)-1-cyano-2-*tert*-butyl-3-phenyl-1-λ^5-phosphirene. This compound consists of a highly distorted square pyramidal arrangement at phosphorus with the cyanide carbon atom occupying the apex; *d*(C–N) is 1.126(6) Å, *i.e.* comparable to that observed for $[\{2,4,6\text{-}(CH_3O)_3C_6H_2\}_3PCN]I$. In addition, the P–CN bond length of the phosphirene, 1.784(4) Å also compares very well with that of $[\{2,4,6\text{-}(CH_3O)_3C_6H_2\}_3PCN]I$, 1.78(2) Å.

During our related studies on compounds of formula R_3PI_2, we have noted that as the basicity of the parent tertiary phosphine is increased, the *d*(I–I) of the charge-transfer complex, $R_3P\text{–}I\text{–}I$, increases [*d*(I–I); Ph_3PI_2, 3.142(4); $PhMe_2PI_2$, 3.408(5) Å].[1] Considering the very high basicity of $[2,4,6\text{-}(CH_3O)_3C_6H_2]_3P$ and the ionic structure of $[\{2,4,6\text{-}(CH_3O)_3C_6H_2\}_3PCN]I$, it occurred to us that the reaction of diiodine with this tertiary phosphine could produce an adduct in which *d*(I–I) is lengthened beyond the sum of the van der Waals radius for diiodine, thus producing an ionic tertiary phosphine diiodine compound, $[R_3PI]I$.

Consequently, we reacted equimolar quantities of $[2,4,6\text{-}(CH_3O)_3C_6H_2]_3P$ with diiodine in diethyl ether solution, equation (2). The product was prepared in quantitative yield

$$[2,4,6\text{-}(CH_3O)_3C_6H_2]_3P + I_2 \xrightarrow[3\text{ d, r.t.}]{Et_2O} [2,4,6\text{-}(CH_3O)_3C_6H_2]_3PI_2 \quad (2)$$

[$C_{27}H_{33}I_2O_9P$: Found (Calc.) C, 41.1 (41.2); H, 4.0 (4.3); I, 32.5 (32.3)%; $^{31}P\text{-}\{H\}$ NMR, singlet δ 64.3]. Recrystallisation of the yellow powder from dichloromethane solution at *ca.* 50 °C produced a large quantity of yellow crystals on standing at room

Table 3 Selected bond lengths (Å) and angles (°) in $[2,4,6\text{-}(CH_3O)_3C_6H_2]_3PI_2$

I(1)–I(2)	3.3394(5)
I(1)–P(1)	2.482(1)
I(1)–I(2)–P(1)	174.52(5)
C(1)–P(1)–I(1)	105.9(1)
C(19)–P(1)–I(1)	106.2(1)
C(10)–P(1)–I(1)	107.1(1)

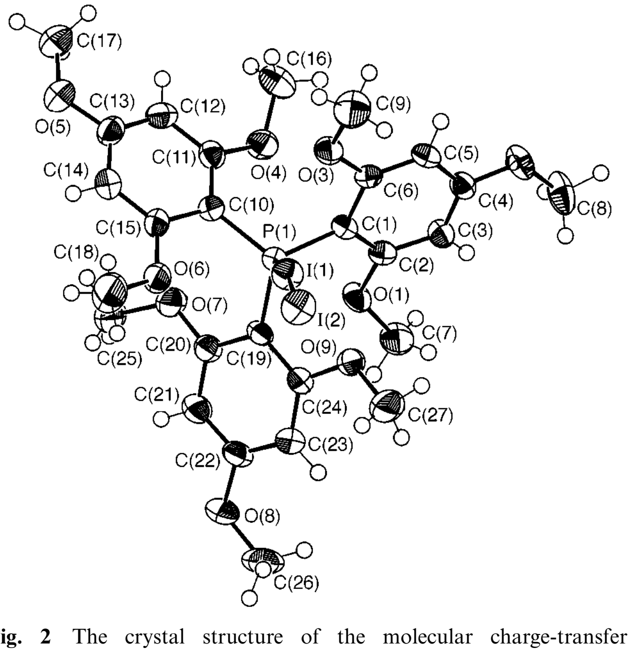

Fig. 2 The crystal structure of the molecular charge-transfer compound $[2,4,6\text{-}(CH_3O)_3C_6H_2]_3PI–I$ (dichloromethane solvent of crystallisation omitted for clarity)

temperature for *ca.* 2 d. In fact, the structure is revealed to be a further example of the molecular four-co-ordinate charge-transfer structure, $[2,4,6\text{-}(CH_3O)_3C_6H_2]_3PI–I{\cdot}CH_2Cl_2$, Fig. 2 (the dichloromethane solvent of crystallisation is omitted for clarity), and not the ionic structure $[\{2,4,6\text{-}(CH_3O)_3C_6H_2\}_3PCNI]I$, which might have been expected with this very basic tertiary phosphine. Selected bond lengths and angles are displayed in Table 3. The *d*(I–I) for the compound, 3.3394(5) Å, is also surprisingly short, less than that exhibited by $PhMe_2PI_2$ [3.408(5) Å] despite the fact that the basicity of $[2,4,6\text{-}(CH_3O)_3C_6H_2]_3P$ is considerably greater than that of $PhMe_2P$. The reason for this phenomenon is unknown but does illustrate that *d*(I–I) for any given R_3PI_2 compound is influenced by factors other than the basicity of R_3P, which we previously thought was solely responsible for *d*(I–I) in R_3PI_2.

X-Ray powder diffraction studies of the compounds R_3PXCN [R = $(CH_3O)_3C_6H_2$, $(CH_3O)_2C_6H_3$, $NCCH_2CH_2$, C_6H_{11} or $PhCH_2$; X = Br or I]

Although we have obtained the crystal structure of the ionic compound $[\{2,4,6\text{-}(CH_3O)_3C_6H_2\}_3PCN]I$, Fig. 1, it occurred to us that other products from the reaction of R_3P and XCN may be present in the solid state, since conceivably, R_3PX_2, $[R_3PX]CN$, $[R_3PCN]X$ and $R_3P(CN)_2$ could all, in theory, be present. We therefore recorded the X-ray powder diffraction patterns of all our R_3PXCN compounds and compared them to the corresponding patterns for R_3PX_2. In all cases, the X-ray powder diffraction patterns for R_3PXCN are completely different to those recorded for R_3PX_2, clearly establishing that in the reaction of XCN with tertiary phosphines, no triorganophosphorus dihalogen compound is produced. The compounds R_3PICN and R_3PBrCN, containing identical R groups, were also compared and again no common diffraction lines were observed. This tentatively suggests that no common species such as $R_3P(CN)_2$ is present in these compounds. The X-ray powder diffraction patterns of $(PhCH_2)_3PX_2$ and $(PhCH_2)_3PXCN$ are compared in Fig. 3.

Solid-state infrared spectroscopic studies

All of the R_3PXCN compounds exhibit two infrared bands at almost identical frequencies, in each case at approximately 2210 and 2070 cm^{-1}. It is known[12] that cyanide exhibits a band in the region 2250–2050 cm^{-1}; the CN stretching band occurs at 2080 cm^{-1} for ionic cyanides and at 2170–2250 cm^{-1} for covalent cyanides. Therefore the infrared band at *ca.* 2070 cm^{-1} observed here can be assigned to CN^- in $[R_3PX]CN$ and the band observed at *ca.* 2210 cm^{-1} can be assigned to PCN in $[R_3PCN]X$. Both Goubeau *et al.*[13] and Miller *et al.*[14] have recorded the infrared spectrum of $P(CN)_3$ and assigned bands at 2204 and 2206 cm^{-1}, respectively, to the carbon–nitrogen stretch. Both groups also assigned a band at *ca.* 600 cm^{-1} to the phosphorus–carbon stretch. Whilst the infrared spectra of all the R_3PXCN compounds do contain a band at *ca.* 590 cm^{-1}, which may be assignable to the phosphorus–carbon stretch, P–CN, all of the compounds contain additional P–C bonds due to the tertiary phosphines which also exhibit an infrared band in this region; therefore, the unequivocal assignment of the band at *ca.* 590 cm^{-1} in R_3PXCN compounds to ν(P–CN) cannot be made with certainty. Interestingly, however, infrared evidence supports the assertion that in the solid state R_3PXCN compounds exist as an approximately stoichiometric mixture of $[R_3PX]CN$ and $[R_3PCN]X$.

$^{31}P\text{-}\{H\}$ NMR solution studies in $CDCl_3$

With the exception of insoluble $(NCCH_2CH_2)_3PXCN$, the $^{31}P\text{-}\{H\}$ NMR spectra of all the R_3PXCN compounds, recorded in $CDCl_3$, exhibit either one or two resonances, *i.e.* suggesting either one or two phosphorus environments. Where two resonances are observed, one is far more intense than the other, the intensity ratio being *ca.* 10 : 1. The chemical shift values and relative intensities of the peaks are listed in Table 4. Previous[1,3] $^{31}P\text{-}\{H\}$ NMR studies of the compounds R_3PX_2 (X = Br or I) in $CDCl_3$ have shown that ionisation occurs to produce $[R_3PX]X$. It follows that, in solution, R_3PXCN compounds may exist entirely as $[R_3PX]CN$ or $[R_3PCN]X$ (one $^{31}P\text{-}\{H\}$ NMR resonance), or as a mixture of both (two NMR resonances) with one species being dominant. The $^{31}P\text{-}\{H\}$ NMR chemical shifts of the corresponding $[R_3PX]X$ compounds are also listed in Table 4. Therefore, by comparing the chemical shift values of the R_3PXCN compounds with those of the corresponding diiodo and dibromo species, identification of $[R_3PI]CN$ and $[R_3PBr]CN$, and thus the cations $[R_3PX]^+$, if present, should be straightforward.

The $CDCl_3$ solutions of the compounds R_3PXCN, Table 4, appear to contain the halogenophosphonium cyanide species, $[R_3PX]CN$, in addition to one other major component, the minor component giving a resonance very similar to those of the analogous halogenophosphonium cation in $[R_3PX]X$[1,3] previously recorded. Interestingly, the $^{31}P\text{-}\{H\}$ NMR spectrum of the $[\{2,4,6\text{-}(CH_3O)_3C_6H_2\}_3PCN]I$ crystals gave a single peak at δ −26.7, *i.e.* identical to the major resonance observed in the $^{31}P\text{-}\{H\}$ NMR spectrum of bulk $[2,4,6\text{-}(CH_3O)_3C_6H_2]_3PICN$, Table 4. This clearly shows that this compound exists predominantly as $[\{2,4,6\text{-}(CH_3O)_3C_6H_2\}_3PCN]I$ in $CDCl_3$ with a small quantity of $[\{2,4,6\text{-}(CH_3O)_3C_6H_2\}_3PI]CN$ also being present. Additionally, the chemical shift value of δ −26.7, corresponding to the cation $[\{2,4,6\text{-}(CH_3O)_3C_6H_2\}_3PCN]^+$, is also observed as the major resonance in the $^{31}P\text{-}\{H\}$ NMR spectrum of $[2,4,6\text{-}(CH_3O)_3C_6H_2]_3PBrCN$, Table 4, indicating that this compound also exists predominantly as the cyanophosphonium bromide species, $[\{2,4,6\text{-}(CH_3O)_2C_6H_2\}_3PCN]Br$, in $CDCl_3$. Indeed, the major resonances for all of the R_3PICN

Table 4 Solution ^{31}P-{H} NMR chemical shifts[a] of R_3PXCN and the corresponding R_3PX_2 compounds in $CDCl_3$

Compound	X = I	$[R_3PI]I^{15}$	X = Br	$[R_3PBr]Br^{15}$
$[2,4,6-(CH_3O)_3C_6H_2]_3PXCN$	−26.7,[b] −64.7	−64.3	−26.7,[b] −52.3	−52.2
$[2,6-(CH_3O)_2C_6H_3]_3PXCN$	−25.9,[b] −72.6	70.7	−25.9,[b] −50.0	−50.2
$(C_6H_{11})_3PXCN$	65.4, 47.5[b]	67.8	105.6, 48.1[b]	105.5
$(PhCH_2)_3PXCN$	35.2	73.7	90.2, 34.1[b]	89.8

[a] δ Values are given in ppm, all shifts recorded relative to 85% phosphoric acid as standard. [b] More intense peak, intensities *ca.* 10:1.

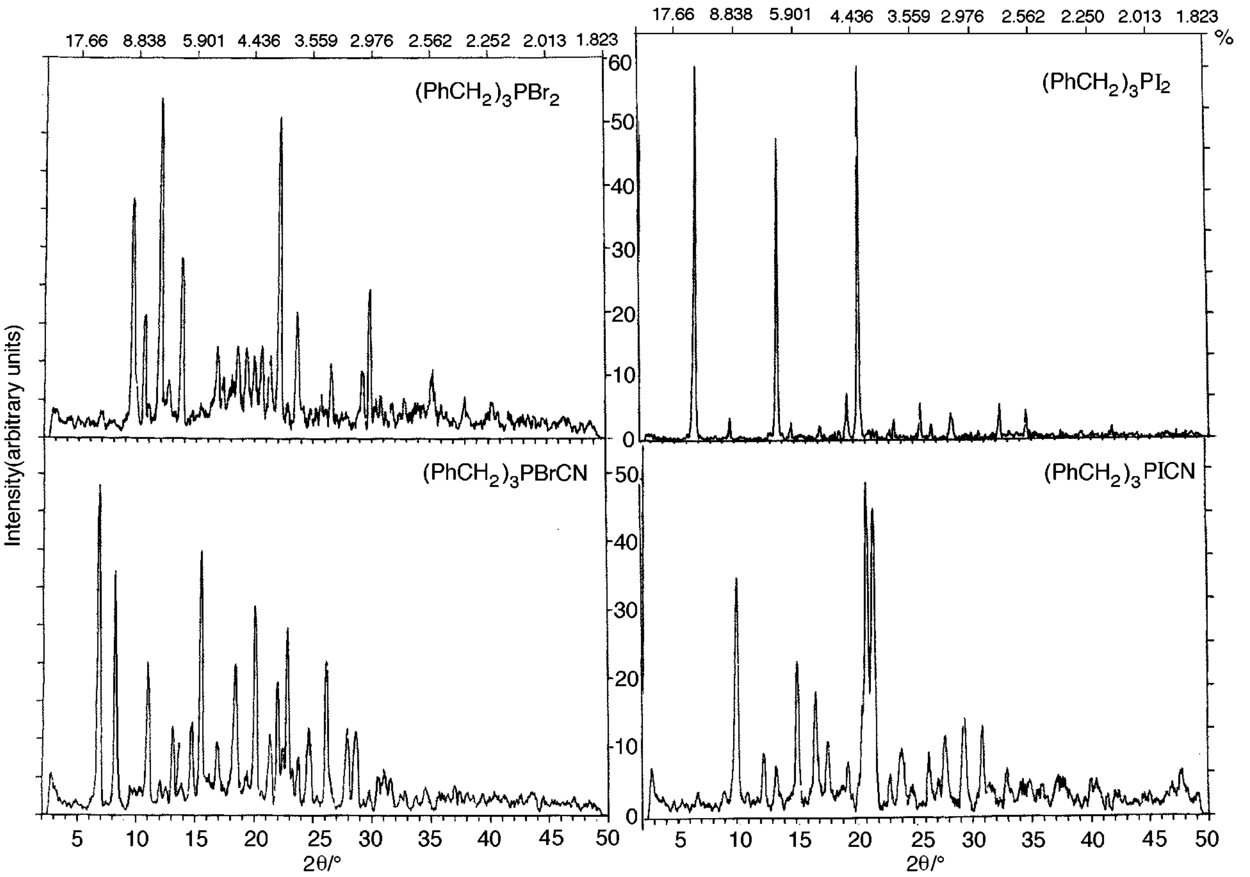

Fig. 3 A comparison of the X-ray powder diffraction patterns of $(PhCH_2)_3PX_2$ and $(PhCH_2)_3PXCN$

compounds are almost identical to those exhibited by the corresponding R_3PBrCN compounds, thus illustrating that $[R_3PCN]X$ is the major component for these species in $CDCl_3$ [and the only component in the case of $(PhCH_2)_3PICN$]. Although there are no previous reports concerning the assignment of a ^{31}P-{H} NMR shift to the species $[R_3PCN]X$, those reported in this work, Table 4, may be made with confidence based on the evidence described herein. Initially, we were sceptical about assigning NMR shifts of δ −25.9 to −48.1 to $[R_3PCN]^+$ since the size and electronegativity of the CN^- anion are intermediate between those of the Cl^- and Br^- anions. It was therefore thought that the ^{31}P-{H} NMR value for $[R_3PCN]^+$ would be between those found for the corresponding $[R_3PCl]^+$ and $[R_3PBr]^+$ species. However, the ^{31}P-{H} NMR shifts found for $[R_3PCN]X$ instead lie in the region more commonly associated with $R_3P{=}O$ compounds.[16] This observation is consistent with the $[R_3PCN]^+$ cation existing as $[R_3P{=}C{=}N]^+$ rather than $[R_3P{-}C{\equiv}N]^+$ in $CDCl_3$.

Conclusion

The reaction of XCN (X = Br or I) with R_3P produces two different ionic products, $[R_3PX]CN$ and $[R_3PCN]X$ with no evidence for the existence of R_3PX_2 or $R_3P(CN)_2$. The crystal structure of $[\{2,4,6-(CH_3O)_3C_6H_2\}_3PCN]I$ is reported and is a major component in the reaction of $[2,4,6-(CH_3O)_3C_6H_2]_3P$ with ICN; however, infrared studies on all of the R_3PXCN compounds indicate that a significant amount of both the cyanotriorganophosphonium halide and the halogenotriorganophosphonium cyanide species are present.

Solution studies of the R_3PXCN compounds in $CDCl_3$ indicate that all of these species exist predominantly as $[R_3PCN]X$ with a minor component assignable to $[R_3PX]CN$ (approximately 10:1 ratio). The crystal structure of $[2,4,6-(CH_3O)_3C_6H_2]_3PI_2$ has also been described and, in contrast to $[\{2,4,6-(CH_3O)_3C_6H_2\}_3PCN]I$ which is ionic, is instead a further example of the molecular four-co-ordinate charge-transfer structure, $R_3PI{-}I$.

Experimental

All of the compounds reported here are moisture-sensitive, consequently, strictly anaerobic and anhydrous conditions were employed for their synthesis. Any subsequent manipulations were carried out inside a Vacuum Atmospheres HE-493 glovebox. Diethyl ether (BDH) was dried by standing over sodium wire for *ca.* 1 d and subsequently refluxed over CaH_2 in an inert atmosphere and distilled directly into the reaction vessel. Anhydrous CH_2Cl_2 was obtained commercially (Aldrich) and used as received. Tertiary phosphines were obtained commercially (Aldrich) and their purity was confirmed prior to use by ^{31}P-{H} NMR spectroscopy. The compounds XCN (X = Br or I) were also obtained commercially (Aldrich) and used as received.

Table 5 Crystallographic data and details of refinement for $[R_3PCN]I$ and R_3PI_2 [R = 2,4,6-$(CH_3O)_3C_6H_2$]

	$[2,4,6\text{-}(CH_3O)_3C_6H_2]_3PCNI$	$[2,4,6\text{-}(CH_3O)_3C_6H_2]_3PI_2 \cdot CH_2Cl_2$
Formula	$C_{29}H_{33}Cl_2INO_9P$	$C_{28}H_{35}Cl_2I_2O_9P$
M	768.33	871.23
Crystal system	Rhombohedral	Monoclinic
Space group	*R*3*c* (no. 161)	*P*2/*c* (no. 14)
a/Å	12.445(2)	14.390(2)
b/Å	—	12.445(2)
c/Å	38.863(4)	19.528(3)
β/°	—	90.84(3)
U/Å^3	5212(1)	3496.8(9)
Z	6	4
D_c/g cm^{-3}	1.469	1.655
F(000)	2328	1720
μ/cm^{-1}	11.70	20.43
Crystal size/mm	0.35 × 0.30 × 0.20	0.35 × 0.35 × 0.25
Maximum 2θ	50.01	49.9
Maximum, minimum transmissions	0.7192, 0.6100	0.6291, 0.5349
Total data measured	2046	6136
No. unique reflections	2046	6136
No. observed reflections [$I > 2.00\sigma(I)$]	1044	6136
No. parameters	142	388
Maximum difference peak, hole/e Å^{-3}	0.692, −1.032	1.182, −1.239
Final *R* indices [$I > 2\sigma(I)$]	0.0475, 0.0917	0.0438, 0.1244
Final *R* indices (all data)	0.1616, 0.1261	0.0666, 0.1329

All of the R_3PXCN (X = Br or I) compounds were synthesised in a similar way, the synthesis of $[2,4,6\text{-}(CH_3O)_3C_6H_2]_3PICN$ being typical; $[2,4,6\text{-}(CH_3O)_3C_6H_2]_3P$ (2.00 g, 2.60 mmol) was suspended in Et_2O (*ca.* 75 cm^3) and subsequently, ICN (0.398 g, 2.60 mmol) was added. After *ca.* 4 d, the resultant solid was isolated using standard Schlenk techniques. The solids were then transferred to pre-dried argon-filled ampoules which were flame sealed.

Elemental analyses were performed by the analytical laboratory of this department and the results are presented in Table 1. The X-ray powder diffraction patterns were recorded on a Scintag XRD2000 powder diffractometer using Cu-Kα radiation (λ = 1.5418 Å). Infrared spectra were recorded as KBr discs on a Perkin-Elmer 783 infrared spectrometer, ^{31}P-{H} NMR spectra on a Bruker AC 200 high-resolution multiprobe NMR spectrometer in $CDCl_3$. All shifts were recorded relative to concentrated phosphoric acid as standard.

Crystallography

Crystals of R_3PI_2 and R_3PICN [R = 2,4,6-$(CH_3O)_3C_6H_2$] were independently mounted in Lindemann tubes under an atmosphere of dry argon. All measurements were performed on a MAC3 CAD4 (R_3PI_2) or a Rigaku AFC6S (R_3PICN) diffractometer employing graphite-monochromated Mo-Kα radiation (λ = 0.710 69 Å) and ω–2θ scans. Both structures were solved by direct methods. Unit cell dimensions were derived from the setting angles of 25 accurately centred reflections. Lorentz-polarisation corrections were applied. Details of the crystallographic measurements and subsequent structure determinations are presented in Table 5. Hydrogen atoms were confined to chemically reasonable positions. Neutral atom scattering factors were taken from ref. 17. Anomalous dispersion effects were taken from ref. 18. The structure determination was performed using SHELXS 86,[19a] and the refinement based on F^2 was performed using SHELXL 93[19b] crystallographic software packages.

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References

1 S. M. Godfrey, D. G. Kelly, A. G. Mackie, C. A. McAuliffe, R. G. Pritchard and S. M. Watson, *J. Chem. Soc.*, *Chem. Commun.*, 1991, 1163; N. Bricklebank, S. M. Godfrey, A. G. Mackie, C. A. McAuliffe, R. G. Pritchard and P. J. Kobryn, *J. Chem. Soc.*, *Dalton Trans.*, 1993, 101; N. Bricklebank, S. M. Godfrey, H. P. Lane, C. A. McAuliffe, R. G. Pritchard and M.-M. Moreno, *J. Chem. Soc.*, *Dalton Trans.*, 1995, 2521.
2 W. W. du Mont, M. Bätcher, S. Pohl and W. Saak, *Angew. Chem.*, *Int. Ed. Engl.*, 1987, **26**, 921.
3 N. Bricklebank, S. M. Godfrey, A. G. Mackie, C. A. McAuliffe and R. G. Pritchard, *J. Chem. Soc.*, *Chem. Commun.*, 1992, 355.
4 F. Ruthe, W. W. du Mont and P. G. Jones, *Chem. Commun.*, 1997, 1947.
5 M. A. HA Al-Juboori, P. N. Gates and A. S. Muir, *J. Chem. Soc.*, *Chem. Commun.*, 1991, 1270; *J. Raman Spectros.*, 1995, **26**, 101.
6 S. M Godfrey, C. A. McAuliffe, R. G. Pritchard and J. M. Sheffield, *Chem. Commun.*, 1996, 2521; S. M. Godfrey, C. A. McAuliffe, R. G. Pritchard, J. M. Sheffield and G. M. Thompson, *J. Chem. Soc.*, *Dalton Trans.*, 1997, 4823.
7 S. M. Godfrey, C. A. McAuliffe, R. G. Pritchard and J. M. Sheffield, *Chem. Commun.*, 1998, 921.
8 N. Bricklebank, S. M. Godfrey, C. A. McAuliffe and R. G. Pritchard, *J. Chem. Soc.*, *Dalton Trans.*, 1993, 2261.
9 K. B. Dillon and J. Lincoln, *Polyhedron*, 1989, **8**, 1445.
10 N. N. Greenwood and A. Earnshaw, *Chemistry of the Elements*, Pergamon Press, Oxford, 1984.
11 M. Ehle, O. Wagner, U. Bergsträßer and M. Regitz, *Tetrahedron Lett.*, 1990, **31**, 3429.
12 K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, Wiley-Interscience, New York, 4th edn., 1986.
13 J. Goubeau, P. Haeberle and H. Ulmer, *Z. Anorg. Allg. Chem.*, 1961, **311**, 110.
14 F. A. Miller, S. G. Franks and O. Ala, *Spectrochim. Acta*, 1965, **21**, 775.
15 J. M. Sheffield, Ph.D. Thesis, UMIST, 1997.
16 R. V. Parish, *NMR*, *NQR*, *EPR and Mössbauer Spectroscopy in Inorganic Chemistry*, Ellis Horwood, London, 1990.
17 *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham, 1974, vol. 4, Table 2.2 A.
18 *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham, 1974, vol. 4, Table 2.3.1.
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