

Structure of R_3PCl_2 compounds in the solid state and in solution: dependency of structure on R. Crystal structures of trigonal bipyramidal $(C_6F_5)_3PCl_2$, $Ph_2(C_6F_5)PCl_2$ and of ionic $Pr^n_3PCl_2$

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A number of triorganophosphorus dichloride compounds R_3PCl_2 , (R_3 = substituted aryl, mixed aryl-alkyl or triaryl) have been synthesized from diethyl ether solution and characterised by analytical and ^{31}P - $\{^1H\}$ NMR data in $CDCl_3$ solution. The majority of the compounds are ionic, $[R_3PCl]Cl$, in $CDCl_3$ solution, in keeping with analogous species containing the heavier halogens $[R_3PX]X$ ($X = Br$ or I), according to ^{31}P - $\{^1H\}$ NMR studies. In contrast, the compounds R_3PCl_2 [$R_3 = (C_6F_5)_3$ or $(C_6F_5)Ph_2$] have a molecular five-co-ordinate trigonal-bipyramidal structure both in $CDCl_3$ solution and in the solid state. The crystal structures of these two compounds have been determined and represent the only crystallographic studies of trigonal-bipyramidal compounds of stoichiometry R_3PCl_2 . The compound $(C_6F_5)_3PCl_2$ exhibits almost perfect trigonal-bipyramidal geometry, whereas $(C_6F_5)Ph_2PCl_2$ shows significant distortion. This may be due to the asymmetry of the equatorial groups around the phosphorus atom. Why R_3PCl_2 [$R_3 = (C_6F_5)_3$ or $(C_6F_5)Ph_2$] adopt a trigonal-bipyramidal structure is reasoned to be due to the acidity of the parent tertiary phosphines, which favours this geometry for the dihalogen adducts, a phenomenon previously observed for dihalogen adducts of tertiary arsines. The crystal structure of $Pr^n_3PCl_2$, the first crystallographically characterised example of an ionic R_3PCl_2 compound which does not contain a solvent molecule, has been found to contain two $Pr^n_3PCl_2$ entities. The first consists of an ionic $[Pr^n_3PCl]^+$ unit weakly linked by a long $Cl \cdots Cl$ contact to a Cl^- , $d(Cl \cdots Cl)$ 3.207(3) Å. The second shows a discrete $[Pr^n_3PCl]^+$ cation, the Cl^- anion being associated with δ^+ H atoms on a $[Pr^n_3PCl]^+$ moiety. This compound was prepared and crystallised from diethyl ether and its relation to the solvated complex $[Ph_3PCl \cdots Cl \cdots ClPPh_3]Cl \cdot CH_2Cl_2$ is discussed.

Despite the familiarity of the reagents R_3PCl_2 and the fact that their existence has been recognised for many years,¹ surprisingly little is known concerning their structural nature, especially in the solid state. In addition, some are widely used chlorinating agents in a variety of organic reactions and Ph_3PCl_2 is commercially available.²

Previous studies on compounds of stoichiometry R_3PCl_2 have mainly concentrated on the nature of such species in solution. Detailed ^{31}P - $\{^1H\}$ NMR investigations³⁻⁶ have concluded that all such species are ionic, $[R_3PCl]Cl$, in MeCN or CH_2Cl_2 solution. These results agree with conductivity studies on Ph_3PCl_2 in MeCN solution by Harris and co-workers,^{7,8} who also concluded an ionic formulation, $[Ph_3PCl]Cl$. In contrast, cryoscopic and spectroscopic measurements⁹ on Ph_3PCl_2 in haloform solvents indicated that 1:1 $Ph_3PCl_2 \cdot YCX_3$ ($Y = H$ or D , $X = Cl$ or Br) adducts were obtained which are reasoned to be molecular dimeric species containing six-co-ordinate phosphorus atoms.

Solid-state investigations into the structure of R_3PCl_2 compounds are much rarer. Dillon and Waddington^{10,11} used high-resolution solid-state ^{31}P - $\{^1H\}$ NMR and NQR spectroscopy to elucidate the structure of Ph_3PCl_2 and its 1:1 adducts with Lewis acids. Both Ph_3PCl_2 and the adducts exhibited a similar NMR resonance, leading these workers to conclude that Ph_3PCl_2 is ionic, $[Ph_3PCl]Cl$, when prepared from MeCN solution. The NQR results supported this conclusion. The compound Me_3PCl_2 has been studied using Raman and IR spectroscopy;¹²⁻¹⁴ the data suggest that Me_3PCl_2 is also ionic in the solid state, $[Me_3PCl]Cl$.

We are involved in a detailed study of compounds of formula R_3EX_2 ($E = P, As$ or Sb ; $X_2 = Cl_2, Br_2, I_2$ or IBr) and have established that where $X_2 = Br_2, I_2$ or IBr the compounds adopt a

novel molecular four-co-ordinate charge-transfer 'spoke' structure, R_3P-X-X ($R = Ph, X_2 = Br_2, I_2$ ^{15,16} or IBr ;¹⁷ $R_3 = PhMe_2, X_2 = I_2$ ¹⁸). On the other hand, other workers have structurally characterised the difluoro-derivatives, Ph_3PF_2 ,^{19,20} and showed them to be molecular trigonal bipyramidal. Until very recently, no compound of formula R_3PCl_2 had been characterised by single-crystal X-ray diffraction; however, we reported²¹ the crystal structure of the compound prepared from the reaction of Ph_3P and dichlorine in dichloromethane solution, which proved to be the solvated product $[Ph_3PCl \cdots Cl \cdots ClPPh_3]Cl \cdot CH_2Cl_2$. This unusual dinuclear species is essentially ionic with long $Cl \cdots Cl$ contacts [3.279(6) Å].

Our related studies²² concerning R_3AsX_2 compounds ($X_2 = Br_2$ or I_2) have shown that the R groups bound to the arsenic centre can have a fundamental effect on the structure of the dihalogen adduct. For example, Ph_3AsBr_2 has a molecular trigonal-bipyramidal structure containing five-co-ordinate arsenic whereas Me_3AsBr_2 has a molecular charge-transfer structure, $Me_3As-Br-Br$ containing four-co-ordinate arsenic. It was reasoned that the acidity of the E atom in any given R_3E species (which is directly affected by R) is responsible for the geometry of any given dihalogen adduct, as well as the identity of the dihalogen adduct itself. If the dihalogen is kept constant, a trigonal-bipyramidal structure for R_3EX_2 ($E = P$ or As) is more likely with increasing acidity of ER_3 ($E = P$ or As). Consequently, it may be possible to synthesize a trigonal-bipyramidal R_3PCl_2 compound with a suitably acidic tertiary phosphine.

The aims of the present study are therefore two-fold. First, since tertiary phosphine dihalide compounds containing the heavier halogens are known to be charge-transfer species, R_3P-X-X ($X_2 = Br_2, I_2$ or IBr) and the difluorides are known to

Table 1 Analytical and spectroscopic data for R₃PCl₂ compounds prepared in Et₂O

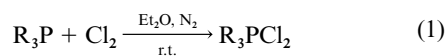
Compound	Colour	Analysis [Found(Calc.)] (%)			³¹ P-{ ¹ H} δ ^a
		C	H	Cl	
Me ₃ PCl ₂	White	24.1 (24.5)	6.6 (6.1)	48.8 (48.3)	72.6
Pr ⁿ ₃ PCl ₂	White	46.7 (46.8)	9.1 (9.1)	30.6 (30.7)	105.9
Pr ⁱ ₃ PCl ₂	White	46.8 (46.8)	8.8 (9.1)	30.3 (30.7)	121.7
Bu ⁿ ₃ PCl ₂	White	52.2 (52.7)	10.4 (9.9)	25.9 (26.0)	103.5
(PhCH ₂) ₃ PCl ₂	White	67.3 (67.2)	5.9 (5.6)	18.6 (18.9)	96.7
(C ₆ H ₁₁) ₃ PCl ₂	White	62.2 (61.5)	9.7 (9.4)	20.5 (20.2)	76.6
(Me ₂ N) ₃ PCl ₂ ^b	White	30.9 (30.8)	7.9 (7.7)	30.5 (30.3)	54.4
(Et ₂ N) ₃ PCl ₂ ^c	White	45.2 (45.3)	9.7 (9.4)	22.1 (22.3)	52.7
(Pr ⁿ ₂ N) ₃ PCl ₂ ^d	White	53.1 (53.7)	12.2 (10.4)	17.1 (17.7)	53.6
Me ₂ PhPCl ₂	White	46.3 (45.9)	5.6 (5.3)	31.9 (33.9)	79.2
MePh ₂ PCl ₂	White	57.8 (57.6)	4.8 (4.8)	25.8 (26.2)	70.3
EtPh ₂ PCl ₂	White	59.6 (58.9)	7.1 (5.3)	24.6 (24.9)	79.5
Ph ₃ PCl ₂	Cream	65.0 (64.9)	4.8 (4.5)	20.9 (21.3)	63.8
(C ₆ F ₅)Ph ₂ PCl ₂	Off-white	51.3 (51.1)	2.6 (4.4)	16.4 (16.8)	-55.8
(C ₆ F ₅) ₃ PCl ₂	White	35.9 (35.8)	0.0 (0.0)	11.8 (11.8)	-104.0
(<i>p</i> -FC ₆ H ₄) ₃ PCl ₂	White	54.8 (55.8)	4.6 (3.1)	17.2 (18.3)	63.9
(<i>p</i> -ClC ₆ H ₄) ₃ PCl ₂	White	49.3 (49.5)	3.0 (2.7)	40.6 (40.7)	62.9

^a All shifts are relative to 85% phosphoric acid standard. ^b 17.6(17.9)% N. 13.0(13.2)% N. ^d 10.4(10.4)% N.

be molecular trigonal bipyramidal, R₃PF₂, is it possible, by varying the R groups on R₃PCl₂, structurally to characterise both trigonal-bipyramidal and four-co-ordinate triorgano-phosphorus dichloride compounds? Secondly, since [Ph₃P·Cl···Cl···ClPPh₃]Cl·CH₂Cl₂ contains a dichloromethane molecule in the structure, the synthesis and crystallographic characterisation of a non-solvated R₃PCl₂ compound would be of interest for comparative purposes.

Results and Discussion

All the triorgano-phosphorus dichlorides synthesized for this study were prepared by the reaction of equimolar quantities of tertiary phosphine and dichlorine in diethyl ether, equation (1)



(r.t. = room temperature). Chlorination of the tertiary phosphine occurred almost immediately and was not only observed by the sudden rise in temperature of the solvent but also by precipitation of the product as a white flocculent solid; the R₃PCl₂ compounds are only sparingly soluble in diethyl ether and are easily isolated using standard Schlenk techniques. All the products described are sensitive to both air and moisture, some intensely so; therefore, strictly anhydrous anaerobic conditions were maintained throughout their synthesis and subsequent characterisation. Elemental analyses of the compounds prepared in Et₂O are given in Table 1 respectively, together with their ³¹P NMR chemical shifts recorded in CDCl₃ solution.

With two notable exceptions, (C₆F₅)₃PCl₂ and (C₆F₅)Ph₂PCl₂, all the R₃PCl₂ compounds exhibit high positive ³¹P-{¹H} NMR resonances. Such resonances are indicative of an ionic structure in CDCl₃ solution, irrespective of their solid-state structure.⁶ Addition of 1 equivalent of AlCl₃ to these R₃PCl₂ compounds, which is known to produce the corresponding ionic [R₃PCl]-[AlCl₄] species,^{3,5,10,11} results in no change in the position of the ³¹P-{¹H} NMR resonance. Furthermore, the values recorded herein for these R₃PCl₂ compounds are in good agreement with those recorded by previous workers,³⁻⁶ who also concluded that such species are ionic, [R₃PCl]Cl. The chemical shifts recorded in Table 1 are also similar to those previously observed for analogous R₃PBr₂²³ and R₃PI₂^{18,24} compounds which have also been shown to adopt the ionic, [R₃PX]X (X = Br or I), structure in CDCl₃ solution. We have previously observed that the CDCl₃ solution ³¹P-{¹H} NMR values for [R₃PBr]Br are slightly more

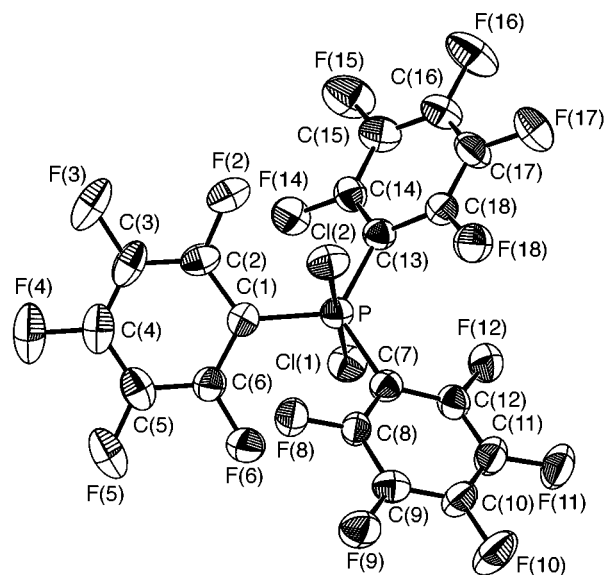


Fig. 1 Crystal structure of molecular trigonal-bipyramidal (C₆F₅)₃PCl₂

positive than those observed for [R₃PI]I. In keeping with this phenomenon, the values recorded here for [R₃PCl]Cl are, in turn, slightly increased compared to those of [R₃PBr]Br. The ³¹P-{¹H} NMR resonances for (C₆F₅)₃PCl₂ and (C₆F₅)Ph₂PCl₂, δ -104.2 and -55.8, respectively, are clearly anomalous and are particularly interesting since they arise from the R₃PCl₂ compounds which contain the most acidic parent tertiary phosphines. Consequently, their structures were investigated by single-crystal X-ray diffraction.

Recrystallisation of R₃PCl₂ [R₃ = (C₆F₅)₃ or (C₆F₅)Ph₂] from dichloromethane solution at room temperature produced a large quantity of colourless crystals on standing for ca. 7 d in each case. In contrast to [Ph₃P·Cl···Cl···ClPPh₃]Cl·CH₂Cl₂²¹ both (C₆F₅)₃PCl₂ and (C₆F₅)Ph₂PCl₂ have a molecular five-coordinate trigonal-bipyramidal structure, Figs. 1 and 2. Selected bond lengths and angles are displayed in Table 2. These compounds represent the first crystallographically characterised R₃PCl₂ compounds which contain five-co-ordinate phosphorus centres and the first examples of non-solvated R₃PCl₂ compounds to be studied by X-ray crystallography. The reason why Ph₃PCl₂ adopts an ionic structure in CH₂Cl₂ whereas both (C₆F₅)₃PCl₂ and (C₆F₅)Ph₂PCl₂ exhibit a trigonal-bipyramidal

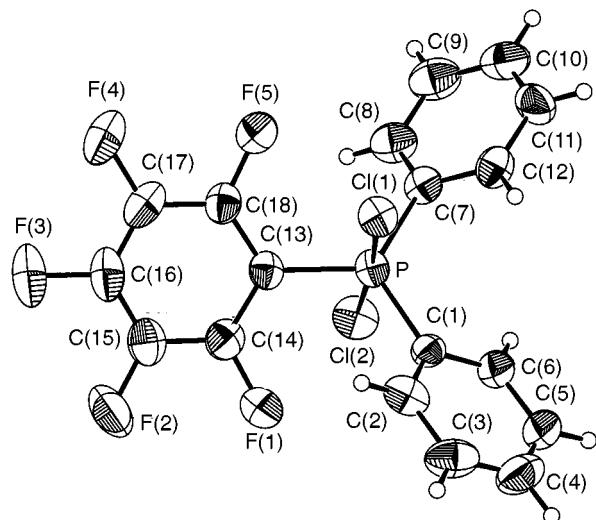


Fig. 2 Crystal structure of molecular trigonal-bipyramidal $(C_6F_5)_3P$ and $(C_6F_5)_2Ph_2P$ dichlorides

Table 2 Selected bond lengths (Å) and angles (°) for R_3PCl_2 [$R_3 = (C_6F_5)_3$ or $(C_6F_5)_2Ph_2$]

	$(C_6F_5)_3PCl_2$	$(C_6F_5)_2Ph_2PCl_2$
Cl(1)–P	2.211(2)	2.244(2)
Cl(2)–P	2.211(2)	2.241(3)
P–C(1)	1.800(5)	1.785(7)
P–C(13)	1.835(5)	1.830(7)
C(1)–P–C(7)	118.9(3)	117.7(3)
C(1)–P–C(13)	118.7(2)	119.6(3)
C(7)–P–C(13)	122.4(3)	122.7(4)
C(13)–P–Cl(2)	89.8(2)	87.6(2)
C(13)–P–Cl(1)	89.8(2)	87.8(2)
Cl(2)–P–Cl(1)	179.13(9)	175.20(11)

structure must be due to the acidity of the parent tertiary phosphine. Since both $(C_6F_5)_3P$ and $(C_6F_5)_2Ph_2P$ are significantly more acidic than Ph_3P for a given solvent, the corresponding dichloride is more likely to adopt a trigonal-bipyramidal structure and indeed this is the case. The less acidic phenyl groups may stabilise the high formal charge on the phosphorus atom in $[Ph_3PCl \cdots Cl \cdots ClPPh_3]Cl \cdot CH_2Cl_2$ such that only a single chloride is needed to attain an energetically favourable state. The inclusion of more acidic C_6F_5 groups necessitates a higher co-ordination number about the central phosphorus atom in order to lower its formal charge.

The compound $(C_6F_5)_3PCl_2$ exhibits nearly perfect trigonal-bipyramidal geometry with identical $d(P-Cl)$ of 2.211(2) Å, Table 2; $(C_6F_5)_2Ph_2PCl_2$ also has very similar $d(P-Cl)$, 2.244(2) and 2.241(3) Å, slightly longer than those of $(C_6F_5)_3PCl_2$ and, more significantly, notable distortion from ideal trigonal-bipyramidal geometry is observed. This probably results from the asymmetric equatorial groups in $(C_6F_5)_2Ph_2PCl_2$, Table 2. Both $(C_6F_5)_3PCl_2$ and $(C_6F_5)_2Ph_2PCl_2$ exhibit longer $d(P-Cl)$ than those of four-co-ordinate $[Ph_3PCl \cdots Cl \cdots ClPPh_3]Cl \cdot CH_2Cl_2$ [$d(P-Cl) = 2.015(9)$ Å], as expected.

In addition to synthesizing the first trigonal-bipyramidal R_3PCl_2 compounds, we were also interested in crystallographically characterising an R_3PCl_2 compound which adopts an ionic structure but doesn't contain a dichloromethane solvent molecule since, as is observed in $[Ph_3PCl \cdots Cl \cdots ClPPh_3]Cl \cdot CH_2Cl_2$, the long-range electrostatic interactions between the solvent and the ionic molecule could influence the product formed. It also occurred to us that no R_3PCl_2 compound containing alkyl groups (and thus greater basicity of the parent tertiary phosphine) has previously been the subject of an X-ray crystallographic study.

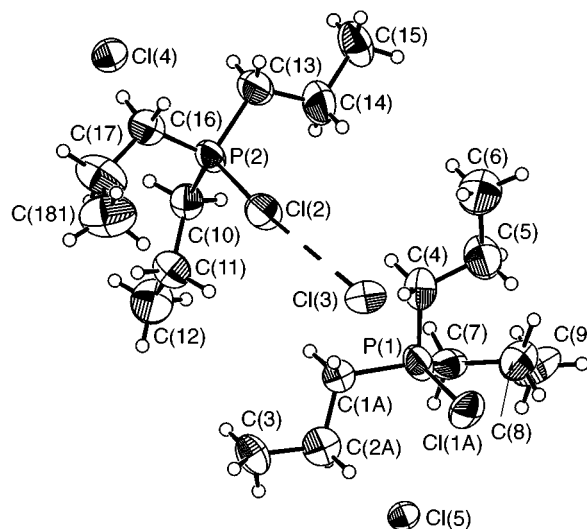


Fig. 3 Crystal structure of ionic Pr^3PCl_2

Table 3 Selected bond lengths (Å) and angles (°) for Pr^3PCl_2

Cl(1A)–P(1)	2.008(9)	P(2)–C(13)	1.789(10)
Cl(2)–P(2)	1.980(3)	P(2)–C(10)	1.790(10)
P(1)–C(4)	1.758(10)	Cl(4) \cdots H(16B)	2.727(6 ^d)
P(1)–C(7)	1.781(12)	Cl(5) \cdots H(7A)	2.528(7 ^h)
C(4)–P(1)–C(7)	114.9(4)	C(13)–P(2)–C(10)	115.6(5)
C(4)–P(1)–Cl(1A)	96.6(5)	C(13)–P(2)–Cl(2)	106.5(4)
C(7)–P(1)–Cl(1A)	117.3(6)	C(10)–P(2)–Cl(2)	106.6(3)

Symmetry relations: I $1 - x, 1 - y, z$; II $-x, 1 - y, z$.

Consequently a sample of Pr^3PCl_2 , prepared in diethyl ether, was recrystallised from the same solvent (and not CH_2Cl_2 , to avoid its possible inclusion in the structure) at room temperature. On standing for *ca.* 7d a large quantity of colourless crystals formed which were removed from the reaction vessel in an inert atmosphere and plunged into an inert oil. From these, a suitable crystal was chosen for examination by single-crystal X-ray diffraction. The structure of Pr^3PCl_2 is illustrated in Fig. 3. Selected bond lengths and angles are displayed in Table 3. Interestingly, the structure is rather complicated, containing two quite different Pr^3PCl_2 entities in the asymmetric unit. In one molecule the Cl^- ion interacts with the chlorine atom of the $[Pr^3PCl]^+$ cation, resulting in a long $Cl \cdots Cl$ contact. This contact, 3.207(3) Å, compares well with those in $[Ph_3P-Cl \cdots Cl \cdots Cl-PPh_3]Cl \cdot 2CH_2Cl_2$, 3.279(6) Å, and represents a significant interaction in the solid state when compared to the dichlorine van der Waals radius (3.6 Å). However, in the other molecule, the Cl^- ion appears to interact with the δ^+ hydrogens on the *n*-propyl groups of the cation. The closest contacts between the δ^+ hydrogens on the cation $[Pr^3PCl]^+$ and the ionic chloride atoms [Cl(4) and Cl(5)] are displayed in Table 3. From Fig. 3 it can also be seen that the two $[Pr^3PCl]^+$ cations are associated with three rather than two Cl^- anions. This is due to the fact that Cl(4) and Cl(5) lie on a mirror plane, effectively contributing half a Cl^- ion each to the asymmetric unit. The $d(P-Cl)$ bond lengths are interesting for several reasons: first they are rather short, 1.980(3) and 2.008(9) Å, slightly shorter than $d(P-Cl)$ in $[Ph_3PCl \cdots Cl \cdots ClPPh_3]Cl \cdot CH_2Cl_2$ [2.015(9) Å]; secondly, and more importantly, it might have been expected that the influence of the long range $Cl \cdots Cl$ contact on P(2)–Cl(2) would serve to weaken the bond. However, this phenomenon is not observed, the P–Cl bond containing the Cl^- contact, 1.980(3) Å, is actually shorter than that with no such contact, 2.008(9) Å. The reason for this remains a mystery but may be related to crystal-packing effects. The structure of Pr^3PCl_2 also does not contain any solvent molecule and is

Table 4 Crystal data and details of refinement for R_3PCl_2 [$R_3 = (C_6F_5)_3$, $(C_6F_5)Ph_2$ or Pr^n]

Empirical formula	$C_{18}Cl_2F_{15}P$	$C_{18}H_{10}Cl_2F_5P$	$C_{18}H_{24}Cl_4P_2$
<i>M</i>	603.05	423.13	462.25
<i>T</i> /K	293(2)	293(2)	183(2)
Crystal system	Monoclinic	Orthorhombic	Orthorhombic
Space group	$P2_1/c$ (no. 14)	<i>Pbcn</i>	<i>Aba2</i>
<i>a</i> /Å	10.380(2)	10.7726(10)	23.132(2)
<i>b</i> /Å	16.835(2)	16.173(2)	11.7264(10)
<i>c</i> /Å	11.354(3)	20.455(2)	19.524(3)
β /°	93.89(3)		
<i>U</i> /Å ³	1979.5(7)	3563.8(7)	5295.9(10)
<i>Z</i>	4	8	8
<i>D</i> /g cm ⁻³	2.024	1.577	1.160
μ /cm ⁻¹	5.55	5.02	5.69
<i>F</i> (000)	1168	1696	1984
Crystal size/mm	0.35 × 0.25 × 0.25	0.35 × 0.30 × 0.25	0.35 × 0.35 × 0.20
Reflections collected	3665	2198	2341
Observed reflections	3450	2197	2324
Parameters	325	235	237
Final <i>R</i> 1, <i>wR</i> 2 indices [<i>I</i> > 2σ(<i>I</i>)]	0.0427, 0.1153	0.0501, 0.1271	0.0608, 0.1471
(all data)	0.1417, 0.1863	0.1385, 0.1720	0.0773, 0.1783

clearly different to that of $[Ph_3PCl \cdots Cl \cdots ClPPh_3] \cdot Cl \cdot CH_2Cl_2$, suggesting that the presence of CH_2Cl_2 could affect the solid-state structure of R_3PCl_2 compounds. The compound $Pr^n_3PCl_2$ also represents the first crystallographically characterised of stoichiometry R_3PCl_2 which adopts an ionic structure and does not contain any solvent.

Conclusion

The results reported clearly show that the majority of R_3PCl_2 compounds are ionic in $CDCl_3$ solution, from ^{31}P - $\{^1H\}$ NMR studies. However for those with very weakly basic (or more acidic) parent tertiary phosphines a trigonal-bipyramidal structure is revealed in the solid state which also persists in $CDCl_3$ solution. It is therefore evident that R_3PCl_2 compounds represent a borderline between two structural types, all reported R_3PF_2 compounds containing five-co-ordinate phosphorus centres^{19,20} and all reported R_3PBr_2 compounds containing four-co-ordinate phosphorus centres. For R_3PCl_2 , however, the co-ordination number for the phosphorus atom is dependent on *R*. This phenomenon has previously been observed for R_3AsBr_2 ,²² Ph_3AsBr_2 , containing the relatively weak base Ph_3As being trigonal bipyramidal whereas Me_3AsBr_2 , containing the stronger base Me_3As , being a molecular four-co-ordinate species, $Me_3As-Br-Br$. The solid-state crystal structure of $Pr^n_3PCl_2$, prepared and recrystallised from Et_2O , is interesting to compare with that of $[Ph_3PCl \cdots Cl \cdots ClPPh_3]Cl \cdot CH_2Cl_2$ prepared and recrystallised from CH_2Cl_2 . Although both of these species are essentially ionic, containing long $Cl \cdots Cl$ contacts, the inclusion of the solvent molecule in the latter compound does appear to affect the nature of the product formed. For $Pr^n_3PCl_2$, no polar solvent molecule is available to stabilise the Cl^- ion resulting in one long Cl^- contact, and the other Cl^- ion being stabilised by the δ^+ hydrogen atoms on a $[Pr^n_3PCl]^+$ cation, Fig. 3.

Experimental

All of the compounds reported here are moisture sensitive, some intensely so, decomposing in a few seconds if exposed to the atmosphere. Consequently, strictly anaerobic and anhydrous conditions were employed for their synthesis. Any subsequent manipulations were carried out inside a Vacuum Atmospheres HE-493 glove-box. 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 and used as received. Tertiary phosphines were

obtained commercially. The purity of all the tertiary phosphines used was confirmed by elemental analysis and ^{31}P - $\{^1H\}$ NMR spectroscopy prior to use. Dichlorine gas was obtained commercially and used as received.

All the R_3PCl_2 compounds were synthesized in a similar way, that of Ph_3PCl_2 being typical. Triphenylphosphine (2.00 g, 7.63 mmol) was suspended in Et_2O (*ca.* 75 cm³) and subsequently dichlorine (0.542 g, 183 cm³, 7.63 mmol) was added. After *ca.* 2 d the resultant white solid was isolated using standard Schlenk techniques. The solids were then transferred to predried 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 ^{31}P - $\{^1H\}$ NMR spectra were recorded as $CDCl_3$ solutions on a Bruker AC200 high-resolution multiprobe spectrometer relative to concentrated phosphoric acid as standard.

Crystallography

Crystals of R_3PCl_2 [$R_3 = (C_6F_5)_3$ or $(C_6F_5)Ph_2$] were independently mounted in Lindemann tubes under an atmosphere of dry argon. Crystals of $Pr^n_3PCl_2$ were submerged in an inert oil under anaerobic conditions and a suitable crystal was chosen by examination under the microscope. The crystal, with its protective coating of oil, was then mounted on a glass fibre and transferred to the diffractometer and cooled to *ca.* 183(2) K in the cold gas stream derived from liquid nitrogen. All measurements were performed on a MAC3 CAD4 diffractometer employing graphite-monochromated Mo-*K* α radiation ($\lambda = 0.71069$ Å) and ω - 2θ scans. All the 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 X-ray measurements and subsequent structure determinations are presented in Table 4. Hydrogen atoms were confined to chemically reasonable positions. Neutral atom scattering factors were taken from ref. 25. Anomalous dispersion effects were taken from ref. 26. All calculations were performed using SHELXS 86 and SHELXL 93 crystallographic software packages.^{27,28} In the crystal structure of $Pr^n_3PCl_2$ one $[Pr^n_3PCl]^+$ cation shows disorder with the chlorine atom and part of a propyl chain occupying two sites in the ratio 0.42(2):0.58(2) [C(1A), C(1A), C(2A):C(1B), C(1B), C(2B)]. Additionally, in the other molecule of $Pr^n_3PCl_2$, which exhibits the long $Cl \cdots Cl$ contact, a terminal CH_3 group semi-populates two sites [C(181) and C(182)].

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