Ionic–Molecular Isomerism in Chlorophenylphosphoranes Ph_nPCl_{5-n} ($1 \leqslant n \leqslant 3$)

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Both ionic and molecular modifications of the three chlorophenylphosphoranes Ph_nPCl_{5-n} ($1 \leqslant n \leqslant 3$) have been isolated for the first time as solids and all have been characterised by elemental analysis, Raman spectroscopy and ^{31}P magic angle spinning (MAS) NMR spectroscopy.

Various types of isomerism are well-known for the halophosphoranes;[1] these include ionic–molecular isomerism accompanying phase change {*e.g.* PF_3Cl_2 which is pseudo trigonal bipyramidal (ψtbp) in the gas phase but $[PCl_4]^+[PF_6]^-$ in the solid} and solid state ionic isomerism (*e.g.* $[PCl_4]^+[PCl_6]^-$ and $[PCl_4]_2{}^+[PCl_6]^-[Cl]^-$).[2] Organochlorophosphoranes are usually either molecular ψtbp, R_nPCl_{5-n}, or ionic, $[R_nPCl_{4-n}]^+[Cl]^-$,[3] but very recently an example of a phase change isomerism was reported in which a molecular form transformed into an ionic solid which for the first time contained both anionic and cationic phosphorus species;[4] $Cl_4P(CH_2Cl)$(c) was formulated as $[Cl_3P(CH_2Cl)]^+[Cl_5P(CH_2Cl)]^-$ on the basis of ^{31}P MAS NMR spectroscopy,[4] analogous to the normal solid-state PCl_5, *viz.* $[PCl_4]^+[PCl_6]^-$.[2] There has been some ambiguity about the nature of the chlorophenylphosphoranes Ph_nPCl_{5-n}($1 \leqslant n \leqslant 3$) in solution.[5] This has arisen largely as a result of (*i*) possible trihalide anion formation, (*ii*) complexation with chlorocarbon solvents and

Table 1 Raman and ^{31}P NMR data for solid Ph_nPCl_{5-n} ($1 \leqslant n \leqslant 3$) species

	$PhPCl_4$	Ph_2PCl_3	Ph_3PCl_2	$[PhPCl_3]^+[Cl]^-$	$[Ph_2PCl_2]^+[Cl]^-$	$[Ph_3PCl]^+[Cl]^-$	Assignment
$\nu(PCl)/cm^{-1\,a}$	268	276	274				$\nu_{sym}(ax)$
				538	567	593	ν_{sym}
	350	335	[c]				$\nu_{sym}(eq)$
	304	297	[d]				$\nu_{asym}(ax)$
				619	607	[e]	ν_{asym}
	525	[e]	[c]				$\nu_{asym}(eq)$
$\delta(^{31}P)^b$	−34.7	[f]	−6.5	76.6	84.1	52.9	

[a] Assignments partly based on comparison with isoelectronic Si species (ref. 10). [b] Spectra recorded at 121.49 MHz under MAS conditions, chemical shifts quoted relative to 85% H_3PO_4. Values consistent with any available data (ref. 6). [c] No equatorial P–Cl bond. [d] Raman inactive. [e] No antisymmetric stretch. [f] Unreliable measurement.

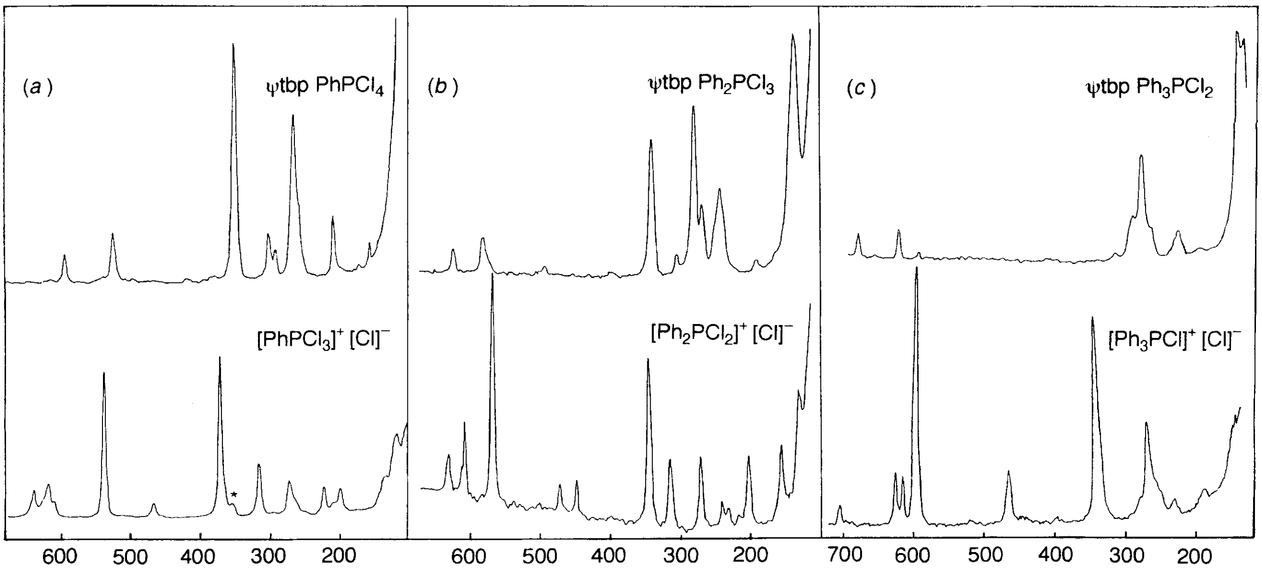

Fig. 1 Comparison of Raman spectra of (*a*) $[PhPCl_3]^+[Cl]^-$ and ψtbp $PhPCl_4$ (* = residual ψtbp $PhPCl_4$), (*b*) $[Ph_2PCl_2]^+[Cl]^-$ and ψtbp Ph_2PCl_3, (*c*) $[Ph_3PCl]^+[Cl]^-$ and ψtbp Ph_3PCl_2

(*iii*) suggested equilibria between ψtbp and ionic species in certain solvents. However, in the solid-state, ^{31}P NMR and ^{35}Cl nuclear quadrupole resonance (NQR) evidence permits both $PhPCl_4$ and Ph_2PCl_3 to be convincingly formulated as ψtbp species whereas Ph_3PCl_2 is ionic, $[Ph_3PCl]^+[Cl]^-$.[6] Clearly there is a fine energetic balance between the two structural types and we have explored various synthetic methods with a view to isolating both ionic and molecular isomers of the chlorophenylphosphoranes in the solid-state.

Accordingly, we have attempted to isolate ionic isomers of $PhPCl_4$ and Ph_2PCl_3 and a ψtbp isomer of Ph_3PCl_2. For the ionic syntheses we have recrystallised the easily prepared (chlorination in toluene) molecular forms of $PhPCl_4$ and Ph_2PCl_3 from anhydrous HCl (−90 °C) and permitted the HCl to evaporate slowly at −10 °C. The intention was to produce the ionic $[Ph_nPCl_{4-n}]^+[HCl_2]^-$ species;[7] subsequent decomposition at the higher temperature would yield the desired $[Ph_nPCl_{4-n}]^+[Cl]^-$ modifications if they possessed sufficient kinetic stability. In the case of $PhPCl_4$, loss of all HCl was spontaneous at −10 °C and left a white solid which rapidly changed (*ca.* 1 h) to the ψtbp form as monitored by chloride analysis and Raman spectroscopy. For Ph_2PCl_3, pumping of the recrystallised solid at −10 °C (10 h) yielded a product for which chloride analysis was consistent with that expected for Ph_2PCl_3 and the Raman spectrum of which clearly showed a set of bands corresponding to the $[Ph_2PCl_2]^+$ cation, as observed for various Lewis acid derivatives. The ionic modification proved to be stable at ambient temperature over a period of months, but warming to *ca.* 180 °C induced some irreversible change to the ψtbp form. The Raman spectra of these ionic modifications are compared with the appropriate ψtbp forms in Fig. 1(*a*) and (*b*).

Passage of chlorine gas through a solution of Ph_3P in toluene yields the well-established ionic solid $[Ph_3PCl]^+[Cl]^-$; the presence of the cation was confirmed in the present work by comparison of the Raman spectrum with those for several Lewis acid salts. However, a milder chlorination (passage of Cl_2 gas over the surface of a solution of Ph_3P in toluene) yielded a white solid whose chloride analysis was in good agreement with that required for Ph_3PCl_2 and whose Raman spectrum is clearly different from that of the ionic species [Fig. 1(*c*)]. The spectrum is consistent with that for a D_{3h} tbp species and shows a good correspondence with that of the well-established Ph_3AsCl_2.[8]

Assignments for the principal P–Cl stretching modes in both the ionic and molecular isomers of all three chlorophenylphosphoranes discussed are shown in Table 1, together with appropriate $\delta^{31}P$ values obtained by MAS NMR; these chemical shifts compare well with any previously available data[6] and generally fall within the predicted 4 and 5 coordination ranges,[9] thus confirming the Raman observations.

A more complete vibrational assignment of these compounds, aided by comparison with isoelectronic chlorophenylsilanes,[10] will be reported elsewhere together with further details of preparations, complexation behaviour and thermochemistry.

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