

Synthesis and Structure of the Phosphorane $P(CH_2Cl)Cl_4$

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The compound $P(CH_2Cl)Cl_4$, which is molecular in the liquid phase, has been shown by solid-state ^{31}P MAS NMR spectroscopy to have the structure $[P(CH_2Cl)Cl_3]^+[P(CH_2Cl)Cl_5]^-$; this is the first example of an organochlorophosphorane having a structure like that of solid $[PCl_4]^+[PCl_6]^-$.

While in theory there are three possible structures open to an organochlorophosphorane R_nPCl_{5-n} , these being molecular pseudo-trigonal bipyramidal (ψ -tbp) (like PF_5), ionic quasi-phosphonium salt $[R_nPCl_{4-n}]^+Cl^-$ (like PBr_5) and ionic $[R_nPCl_{4-n}]^+[R_nPCl_{6-n}]^-$ (like the normal room temperature

form of PCl_5), no example of the third structure has been observed in the solid state. When R is a simple alkyl group such as Me or Et, the compounds all have quasi-phosphonium salt structures, irrespective of the value of n .¹ When R = Ph the compounds are molecular for $n = 1$ or 2 with equatorial

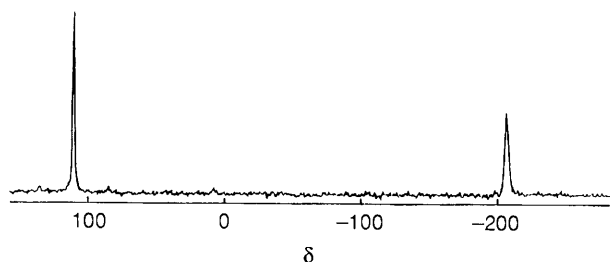


Fig. 1 ^{31}P MAS NMR Spectrum of $\text{P}(\text{CH}_2\text{Cl})\text{Cl}_4$ at 258 K (500 pulses; cross-polarisation; relaxation delay 1 s; spin rate 3000 Hz; operating frequency 121.421 MHz)

phenyl groups, while for $n = 3$ the PBr_5 structure is again found.¹ The more electronegative C_6F_5 group takes up an axial position in the ψ -tbp structure of $\text{P}(\text{C}_6\text{F}_5)\text{Cl}_4$,^{2,3} and $\text{P}(\text{CCl}_3)\text{Cl}_4$ has also been shown to have a molecular structure, with an axial CCl_3 group.^{4,5} These results indicate that a change of structure occurs between PMeCl_4 and $\text{P}(\text{CCl}_3)\text{Cl}_4$, and it was therefore of considerable interest to prepare and characterize structurally the intermediate species $\text{P}(\text{CH}_2\text{Cl})\text{Cl}_4$ and $\text{P}(\text{CHCl}_2)\text{Cl}_4$.

The phosphorane $\text{P}(\text{CH}_2\text{Cl})\text{Cl}_4$ was synthesised by careful chlorination (as monitored by ^{31}P NMR spectroscopy) of $\text{P}(\text{CH}_2\text{Cl})\text{Cl}_2$, which was obtained by the method of Prishchenko *et al.*⁶ [Excess of chlorine must be avoided, or $\text{P}(\text{CCl}_3)\text{Cl}_4$ would result.⁴] Removal of the solvent *in vacuo* gave the phosphorane as a viscous milky liquid, which slowly solidified on standing at room temperature. The ^{31}P spectrum of the liquid consisted of a single resonance at $\delta -39.0$, readily ascribed to the molecular (ψ -tbp) form. The presence of the CH_2Cl group was confirmed by recording the ^1H and ^{13}C undecoupled NMR spectra J_{CH} 167.6, J_{CP} 118.5 Hz, and the identity of the compound was established by elemental analysis for chlorine. The solid-state ^{31}P MAS spectrum of a freshly-prepared sample of the phosphorane, recorded at 258

K to bring it all into the solid form, is shown in Fig. 1, and consists of two signals at δ 111.1 and -206.1 , assignable to the $[\text{P}(\text{CH}_2\text{Cl})\text{Cl}_3]^+$ and $[\text{P}(\text{CH}_2\text{Cl})\text{Cl}_5]^-$ ions respectively. Hence, the solid state structure at this temperature is akin to that of $[\text{PCl}_4]^+[\text{PCl}_6]^-$, and represents the first example of an organochlorophosphorane with the $[\text{PRCl}_5]^-$ ion as part of its normal structure.

These shift assignments were confirmed by recording the solution-state spectra of $[\text{P}(\text{CH}_2\text{Cl})\text{Cl}_3]^+[\text{AlCl}_4]^-$ [^{31}P δ 112.4 (CH_2Cl_2)], $[\text{P}(\text{CH}_2\text{Cl})\text{Cl}_3]^+[\text{SbCl}_6]^-$ [^{31}P δ 111.0 (PhNO_2)] and $[\text{NEt}_4]^+[\text{P}(\text{CH}_2\text{Cl})\text{Cl}_5]^-$ [^{31}P δ -206.8 (CD_3NO_2)]. The phosphorane reverts to the molecular form when dissolved in CH_2Cl_2 or CDCl_3 , just like PCl_5 itself.

The compound decomposes slowly, even when stored in a sealed container under N_2 , giving various phosphorus-containing species including PCl_3 and PCl_6^- . This shows that the P-C bond is not very strong, as observed previously in $\text{P}(\text{CCl}_3)\text{Cl}_4$ ^{4,7,8} and $\text{P}(\text{C}_2\text{Cl}_5)\text{Cl}_4$.⁴ Further studies on this compound, its decomposition route and its derivatives are in progress.

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