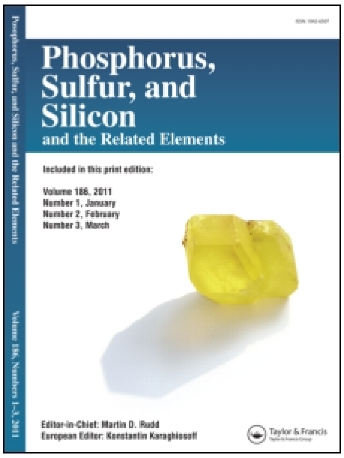

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Structure, Stability and Reactivity of Some 4-, 5- and 6- Coordinate Phosphorus (V) Compounds

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STRUCTURE, STABILITY AND REACTIVITY OF SOME 4-, 5- AND 6-COORDINATE PHOSPHORUS (V) COMPOUNDS

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Abstract The preparation and structures of several phosphoranes containing ortho-substituted aromatic groups are described, together with their reactivity towards some Lewis acids and bases. Results are also presented for CH_2ClPCl_4 and $CHCl_2PCl_4$.

Competing steric and electronic effects have been proposed in order to rationalise previous interesting results obtained by our research group for reactions of excess AgCN with $RPCl_5^-$ (R=Cl or various organo-substituents),[1-3] where the products depended on the nature of R, as summarised below.

PCl_6^-		$\xrightarrow{AgCN(xs)}$	$[PCl_3(CN)_3]^-$	(both isomers)
$RPCl_5^-$	(R=Ph, CCl_3)	$\xrightarrow{AgCN(xs)}$	$[RPCl_2(CN)_3]^-$	(all three isomers)
$RPCl_5^-$	(R=Me, Et)	$\xrightarrow{AgCN(xs)}$	$[RP(CN)_5]^-$	
$RPCl_5^-$	(R=C_6F_5)	$\xrightarrow{AgCN(xs)}$	$[RPCl(CN)_4]^-$	(one isomer only)

The mechanism of substitution is thought to involve dissociation of a chloride ion from the anionic complex to yield a phosphorane, equation (1), followed by addition of cyanide ions, equation (2).

$$[RPCl_5]^- \rightleftharpoons RPCl_4 + Cl^- \qquad (1)$$

$$RPCl_4 + CN^- \rightarrow [RPCl_4(CN)]^- \qquad (2)$$

etc.

Electronically, the presence of electronegative R groups should help to delocalise the formal negative charge on phosphorus, and tend to prevent dissociation, thus hindering further substitution, as shown by the difference in reaction products for R=Me and CCl_3. The exception to this generalisation appears to arise when R is C_6F_5, which is more electronegative than Ph, but substitution still proceeds one stage further. This behaviour could be due to a steric effect, with the bulkier C_6F_5 group being more easily accommodated in a 5-coordinate (Ψ-tbp) than in a 6-coordinate (Ψ-octahedral) structure, thus favouring more extensive dissociation to the phosphorane. To test these postulates further, we planned to synthesise six-coordinate ions $RPCl_5^-$ with sterically hindered R groups, and study their reactions with AgCN.

Several aryl phosphoranes $RPCl_4$ with bulky ortho-substituents have been prepared by chlorination of the corresponding phosphanes, and characterised structurally by ^{31}P NMR and (in some cases) ^{35}Cl NQR spectroscopy. In all instances these compounds had molecular (Ψ-tbp) structures, though the position of the R group varies with its electronegativity. T-dependence studies of the NQR of $(2,4,6\text{-}(CF_3)_3C_6H_2)PCl_4$ ($ArPCl_4$) have shown a phase transition at 190.5 ± 0.5 K. The structural conclusions have been confirmed by preparing derivatives containing $RPCl_3^+$ ions via reaction with strong Lewis acids such as BCl_3 or $SbCl_5$, and recording their spectroscopic parameters. It was found, however, that ortho-substituents such as CH_3, CF_3 or even Cl on the aryl group in $RPCl_4$ inhibit the formation of $RPCl_5^-$, since no initial reaction with R'_4NCl was apparent from the ^{31}P NMR spectra in either CH_2Cl_2 or $PhNO_2$. Over a period of hours or days there was a slow reduction to the analogous phosphane $RPCl_2$, possibly assisted by the formation of the trichloride ion, equation (3).

$$RPCl_4 + Cl^- \rightarrow RPCl_2 + Cl_3^- \qquad (3)$$

Attempts were also made to obtain six-coordinate cyano-species by direct reaction of $RPCl_4$ with R'_4NCN, but reduction to $RPCl_2$ was again observed, probably accompanied by the formation of cyanogen chloride, equation (4).

$$RPCl_4 + R'_4NCN \rightarrow RPCl_2 + CNCl + R'_4NCl \qquad (4)$$

While these results support the hypothesis that bulky substituents favour 5- over 6-coordination in phosphorus, they did not assist directly our main objective. They indicated, however, that it would be worthwhile to ascertain whether the presence of more than one bulky group would influence significantly the structure found for R_2PCl_3, where various possibilities exist. These phosphoranes could be molecular, like $RPCl_4$, or else they could have the ionic quasi-phosphonium salt structure $R_2PCl_2^+Cl^-$, if steric and/or electronic considerations favour 4- rather than 5-coordination. The materials were again prepared by chlorination of the appropriate phosphanes.

The results for R=2-MeC_6H_4, mesityl or 2,6-$(CF_3)_2C_6H_3$ support ionic structures for these compounds in both solution and solid state. For R=2-$CF_3C_6H_4$, an equilibrium between 4- and 5-coordinate forms appears to exist in solution, although the NMR data support an ionic structure for the solid. The results for R=C_6Cl_5 were more equivocal, but suggest an ionic formulation. The most interesting results were those for chlorination of the phosphane Ar_2PCl (Ar=2,4,6-$(CF_3)_3C_6H_2$), which did not lead to the expected phosphorane, but to cleavage of a P-C bond, with formation of ArCl and $ArPCl_4$ (equation 5), both positively identified. The same reaction products were observed, together with some unreacted phosphane, when less than a stoichiometric quantity of chlorine was used. The phosphane was not oxidised by the milder chlorinating agent PCl_5, although a possible cationic species $Ar_2PCl_2^+$ (as its hexachloroantimonate) was detected from reaction with $SbCl_5$. There was thus no evidence for the formation of Ar_2PCl_3. Similarly, the phosphane $ArP(C_6F_5)Cl$ reacted with chlorine to yield ArCl and $P(C_6F_5)Cl_4$, again with cleavage of a P-C bond. With ArP(Ph)Cl, however, the results after chlorination suggest an equilibrium between molecular and ionic structures for the phosphorane in solution, and no P-C bond scission. Addition of $SbCl_5$ gave the expected ionic product. Rationalisation of the results obtained for these various systems will be proposed.

$$Ar_2PCl + 2Cl_2 \rightarrow ArPCl_4 + ArCl \qquad (5)$$

It was also of interest to investigate the structures and reactions of the phosphoranes CH_2ClPCl_4 and $CHCl_2PCl_4$, since $MePCl_4$ is ionic in the solid state $(MePCl_3^+Cl^-)^4$, whereas CCl_3PCl_4 is molecular, with the CCl_3 group axial.[5] These species were synthesised successfully, although $CHCl_2PCl_4$ could not be obtained in a completely pure state, a small quantity of CCl_3PCl_4 being present. This did not interfere with structural elucidation since its spectroscopic properties had already been established.[3,6] The phosphorane CH_2ClPCl_4, while molecular in the liquid state, solidified to a product with the unique structure $[CH_2ClPCl_3]^+ [CH_2ClPCl_5]^-$, as shown by solid state ^{31}P NMR,[7] and confirmed by preparing separate derivatives containing both constituent ions. The compound $CHCl_2PCl_4$ is molecular in both solid and solution, like CCl_3PCl_4. It reacted with excess chloride ions to form the $[CHCl_2PCl_5]^-$ ion, which could be substituted with AgCN, giving cyano-derivatives. Complete reaction through to $[CHCl_2P(CN)_5]^-$ was observed with excess AgCN, and isomeric configurations for the intermediate species were assigned by the method of pairwise interactions.[1-3,8,9] The pattern of substitution proved to be identical to that found for the reaction of $[EtPCl_5]^-$ with cyanide ions.[3]

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