Synthesis and Properties of New Dichlorophosphinothioyl-derivatives of Amines

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Dichlorophosphinothioyl-derivatives of amines, $[Cl_2P(S)]_2NR$ and $Cl_2PS{\cdot}NR{\cdot}PCl_2$ (R = Me, Et, or Ph), have been prepared by reactions of the bis(dichlorophosphino)-amines, $(Cl_2P)_2NR$ (R = Me, Et, or Ph), with elemental sulphur in the presence of anhydrous aluminium chloride. The compounds $Cl_2P(S){\cdot}NR{\cdot}PCl_2$ eliminate PCl_3 when heated leaving cyclodiphosphazanes, $[R{\cdot}NP(S)Cl]_2$. Dichlorophosphinothioyl(dichlorophosphinyl)-amines, $Cl_2P(S){\cdot}NR{\cdot}P(O)Cl_2$ (R = Me, Ph) and bis(dichlorophosphinothioyl)amines, $[Cl_2P(S)]_2NR$ (R = Me, Ph), have been prepared by the condensation of $Cl_2P(S){\cdot}NHR$ with $P(O)Cl_3$ or $P(S)Cl_3$ respectively in the presence of triethylamine. All the above compounds were unreactive to anhydrous hydrogen chloride at atmospheric pressure. The ^1H and ^{31}P n.m.r. and i.r. spectra of these compounds are discussed.

THE synthesis of dichlorophosphinyl-derivatives of methylamine $Cl_2P(X){\cdot}NMe{\cdot}P(Y)Cl_2$ (X = Y = O; X = O, Y = S; X = O, Y = lone pair) from the condensation reactions of phosphoryl chlorides, and from the reactions of phosphoryl chlorides with heptamethyldisilazane was recently reported.[1] The analogous fluorides $F_2P(X)NMeP(Y)F_2$ (X = Y = O [2]; X = Y = S [2]; X = O; Y = S [3]; X = O, Y = lone pair [4]) have also been recently prepared. Other compounds of related structure include the diphenylphosphinothioyl-amines $[Ph_2P(S)]_2NR$ (R = H[5], alkyl [5,6]) and alkoxyphosphinothioyl-amines $[(EtO)_2P(S)]_2NR$ (R = Alkyl) [7] which have been known for some time. However, bis-(dichlorophosphinothioyl)-derivatives of amines are not readily accessible by the routes to the chlorides above because of difficulties encountered in the preparation of the methylamino-derivative $Cl_2P(S)NHMe$ and because of the lack of reactivity of silicon–nitrogen compounds towards thiophosphoryl chlorides.[1]

We have found that the dichlorophosphinothioyl-derivatives $[Cl_2P(S)]_2NR$ (R = alkyl or aryl) are conveniently obtained by oxidation of the analogous phosphorus(III)-compounds $(Cl_2P)_2NR$ [8,9] with elemental sulphur. Phosphorus(III) trihalides are relatively unreactive towards elemental sulphur, but it is known [10] that anhydrous aluminium chloride will catalyse the sulphuration reaction. In the case of the di(phosphino)amines $(Cl_2P)_2NR$ there was no reaction with sulphur alone at temperatures up to *ca.* 200°, but sulphuration was found to proceed fairly smoothly at lower temperatures (*ca.* 150°) in the presence of small quantities of anhydrous aluminium chloride. Both mono- and di-sulphides were formed, and the P–N bonds were left intact:

$$(Cl_2P)_2NR \xrightarrow{S_8/AlCl_3} Cl_2P{\cdot}NR{\cdot}P(S)Cl_2 \xrightarrow{S_8/AlCl_3} [Cl_2P(S)]_2NR$$

This result may be compared with that obtained in the sulphuration of the more reactive phenylphosphinoamines $(Ph_2P)_2NR$[6] and $(Ph_2PNR)_2PPh$ (R = Me, Et) [11] where no monosulphides have been reported. The reaction proceeds more readily when R = alkyl than when R = phenyl, which suggests that the base strength of the phosphine is important in determining the ease of reaction, as is found in the uncatalysed sulphuration of simple phosphines PR_3.[12]

The disulphides $[Cl_2P(S)]_2NR$ are thermally and hydrolytically relatively stable; hydrolysis was only apparent after several weeks exposure to air. However, the monosulphides $Cl_2P{\cdot}NR{\cdot}P(S)Cl_2$ (R = alkyl), hydrolyse fairly readily in air and on prolonged heating loose phosphorus trichloride at *ca.* 200 °C, leaving cyclodiphosphazanes $[ClP(S)NR]_2$:

$$2Cl_2P(S){\cdot}NR{\cdot}PCl_2 \longrightarrow [ClP(S)NR]_2 + 2PCl_3$$

Some of these cyclodiphosphazanes have previously been obtained [13] by the reactions:

$$(Cl_3PNR)_2 + 2H_2S \xrightarrow{\text{pyridine}} [ClP(S)NR]_2 + 4HCl \ (R = Me, Ph)$$

The monosulphides, $Cl_2P(S){\cdot}NR{\cdot}PCl_2$, were frequently contaminated with the cyclodiphosphazanes, especially when R = Me, presumably as a result of their thermal instability. The *N*-phenyl derivative $Cl_2P(S){\cdot}NPh{\cdot}PCl_2$ was only tentatively identified by ^{31}P n.m.r.

The decomposition of the monosulphides may proceed through the formation of a four-centred intermediate of the type shown (Figure), followed by the elimination of phosphorus trichloride either in a stepwise, or in a concerted manner. The disulphides $[Cl_2P(S)]_2NR$ could also form cyclodiphosphazanes by elimination of thiophosphoryl chloride, but this was not observed at temperatures up to *ca.* 250°. The rate of formation of an intermediate such as that shown may be

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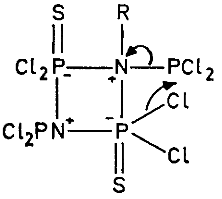
expected to be dependent on the base strength of the bridging nitrogen atom. The greater thermal stability of the derivatives $[Cl_2P(S)]_2NR$ would therefore be consistent with the assumption, on the basis of simple electronegativity effects, that the nitrogen atom in $[Cl_2P(S)]_2NR$ is more weakly basic than that in $Cl_2P(S){\cdot}NR{\cdot}PCl_2$. Clearly this is not the only factor determining the rate of PCl_3 or $PSCl_3$ elimination, but it would be interesting to see whether the effects of other substituents of differing electronegativity can be accounted for in the same way.



Possible intermediate in the thermal decomposition of $Cl_2P(S){\cdot}NR{\cdot}PCl_2$

TABLE 1

N.m.r. data

Compound	¹H				³¹P	
	τCH_3	τCH_2	$J_{P\text{-}N\text{-}C\text{-}H}$(Hz)	$J_{H\text{-}C\text{-}C\text{-}H}$(Hz)	Shift	$J_{P\text{-}N\text{-}P}$
$[Cl_2P(S)]_2NMe$	6·50		14·9		−47·2	
$[Cl_2P(S)]_2NEt$	8·45	5·70	20·3	6·5	−45·0	
$[Cl_2P(S)]_2NPh$					−43·5	
$Cl_2P(S)NMePCl_2$ *	7·08		15·7 †		−51·4 †	122
			1·2		−167·7	
$Cl_2P(S)NEtPCl_2$	8·48	6·00	22·3 †	6·5	−51·7 †	118
			1·0		−169·8	
$Cl_2P(S)NPhPCl_2$ §					−49·9 †	126
					−162·7	
$Cl_2P(O)NMeP(S)Cl_2$ *	6·54		13·7		−10·4	3 ‡
			16·2 †		−49·4 †	
$Cl_2P(O)NPhP(S)Cl_2$					−7·6	30
					−45·3 †	
$[ClP(S)NMe]_2$	7·06		16·6		−52 ¶	
$[ClP(S)NEt]_2$	8·56	6·56	18·4	7·1	−47·9(2) ¶	
					−49·0(1)	
$Cl_2P(S)HNMe$	7·03		20·4		−60·9	
$Cl_2P(S)NHPh$					−48·0	

* From reference 1. † Involving ³¹P nucleus in $-P(S)Cl_2$ group. ‡ Measured on a Jeol C60HL spectrometer with a spinning 8 mm tube; $^1H\{^{31}P\}$ heteronuclear tickling experiments gave $J_{P\text{-}N\text{-}P} = 4 \pm 2$ Hz on a Jeol C60H spectrometer. § Tentative assignments. ¶ Two geometrical isomers; figures in parentheses indicate relative intensity.

By analogy with previous work,[1] dichlorophosphinothioyl-derivatives $Cl_2P(S){\cdot}NHR$ (R = Me,[14] Ph [15]) were expected to give di(phosphinothioyl)amines with thiophosphoryl chloride, but attempts to obtain dichlorophosphinothioylmethylamine by reaction of methylamine hydrochloride with thiophosphoryl chloride [14] were unsuccessful. It was eventually obtained in low yield from these reactants in the presence of sodium hydroxide, with the latter in aqueous solution.[16] $Cl_2P(S){\cdot}NHPh$ was readily prepared as previously described [15] and the two bis(dichlorophosphinothioyl)-derivatives identified from the reactions:

$$Cl_2P(S){\cdot}NHR + PSCl_3 \xrightarrow{Et_3N} [Cl_2P(S)]_2NR + HCl\ (R = Me, Ph)$$

The *N*-phenyl compound was only obtained in low yield.

The dichlorophosphinothioyl-derivatives $Cl_2P(S)NHR$ (R = Me, Ph) also gave good yields of the oxide–sulphides on reaction with phosphoryl chloride:

$$Cl_2P(S){\cdot}NHR + POCl_3 \xrightarrow{Et_3N} Cl_2P(S){\cdot}NR{\cdot}P(O)Cl_2 + HCl$$

These same products could not, however, be obtained by the condensation of dichlorophosphinylamines $Cl_2P(O){\cdot}NHR$ (R = Me, Ph) with thiophosphoryl chloride in the presence of triethylamine. These, and previous observations,[1,17] show that the substrates for this type of reaction need to be good electrophiles to avoid side reactions such as the self-condensation of derivatives of the type $Cl_2P(X){\cdot}NHR$ (X = O or S).

All the phosphinothioyl-derivatives noted above were unreactive to anhydrous hydrogen chloride in methylene chloride solution at atmospheric pressure. This suggests that these compounds are generally only weakly basic, for phosphorus–nitrogen bonds are generally cleaved by hydrogen chloride in more basic phosphorus(v) amides.[18] This lack of reactivity, especially in the dithiocyclodiphosphazanes above, may be contrasted with the ready cleavage [19] of the P–N ring in the dioxocyclodiphosphazanes $[ClP(O)NR]_2$ by hydrogen chloride to give derivatives of the type $Cl_2P(O){\cdot}NR{\cdot}P(O)ClNHR$, but

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in the latter case the activation energy for the reaction may be lowered by the ease of formation of a five co-ordinated phosphorus atom in the transition state. The apparent weakly basic nature of the *N*-phenyl-derivative $Cl_2P(O){\cdot}NPh{\cdot}P(S)Cl_2$ is consistent with the fact that its crystal structure reveals [20] a near planar distribution of bonds about the nitrogen atom, indicating a conjugative interaction between the nitrogen lone-pair and the phosphorus atoms.

TABLE 2

I.r. data

Compound	ν(C–N) cm^{-1}	ν_{as}(P–N–P) cm^{-1}	ν(P–S), ν_{sym}(P–N–P) cm^{-1}
$(Cl_2P)_2NMe$ ‡	1169, 1092	828	634
$Cl_2P{\cdot}NMe{\cdot}P(S)Cl_2$ *	1067	855	750
$[Cl_2P(S)]_2NMe$ †	1021	870	772, 735
$Cl_2P(S){\cdot}NMe{\cdot}P(O)Cl_2$ †	1039, 1026	885	733
$Cl_2P{\cdot}NEt{\cdot}P(S)Cl_2$ *	1046	878	767, 735
$[Cl_2P(S)]_2NEt$ *	1008	918, 892	768, 748, 720
$[Cl_2P(S)]NPh$ †	?	902, 890	759, 739
$Cl_2P(S){\cdot}NPh{\cdot}P(O)Cl_2$ †	?	908, 896	741

* Obtained from liquid films. † Obtained from Nujol mulls. ‡ From ref. 8; sample in CCl_4–hexane solution.

TABLE 3

Summary of routes to the remaining dichlorophosphinothioyl-derivatives

Reactant(s) (mol)	Conditions	Purified by	Product(s)	Yield (%)	M.p./b.p. °C (mmHg)
$(Cl_2P)_2NEt$ (0·10), S (0·10), $AlCl_3$ (*ca.* 0·005)	*ca.* 150 °C	Vacuum dist.	$Cl_2P(S)NEt{\cdot}PCl_2$	78	80—82 (0·2)
$(Cl_2P)_2NEt$(0·37), S (0·74), $AlCl_3$ (*ca.* 0·01)	*ca.* 150 °C	Vacuum dist.	$[Cl_2P(S)]_2NEt$	92	90—94 (0·2)
$(Cl_2P)_2NPh$ (0·019), S (0·019), $AlCl_3$ (*ca.* 0·001)	*ca.* 200 °C		$Cl_2P(S){\cdot}NPh{\cdot}PCl_2$ tentatively identified by ^{31}P n.m.r.		
$(Cl_2P)_2NPh$ (0·31), S (0·62), $AlCl_3$ (*ca.* 0·01)	*ca.* 200 °C	Cryst. from Et_2O–light petroleum (b.p. 40—60°) (1 : 1)	$[Cl_2P(S)]_2NPh$	56	64—65
$Cl_2P(S){\cdot}NEt{\cdot}PCl_2$ (0·022)	*ca.* 200 °C	Cryst. from Et_2O	$[ClP(S)NEt]_2$ (two geometrical isomers)	43	75—80 (0·1)
$[Cl_2P(S)]_2NMe$ (0·006)	*ca.* 250 °C		$[Cl_2P(S)]_2NMe$		
$[Cl_2P(S)]_2NEt$ (0·013)	*ca.* 250 °C		$[Cl_2P(S)]_2NEt$		
$Cl_3P(O)$ (0·040), $Cl_2P(S){\cdot}NHMe$ (0·040), Et_3N (0·040)	*ca.* 20 °C ether (75 ml)	Cryst. from Et_2O–pentane (1 : 1)	$Cl_2P(O){\cdot}NMe{\cdot}P(S)Cl_2$	54	84—85
$Cl_3P(S)$ (0·015), $Cl_2P(S){\cdot}NHMe$ (0·015), Et_3N (0·015)	*ca.* 20 °C in ether (40 ml)	Cryst. from light petroleum (b.p. 40—60°)	$[Cl_2P(S)]_2NMe$	83	61—62
$Cl_3P(S)$ (0·19), $Cl_2P(S){\cdot}NHPh$ (0·19), Et_3N (0·19)	*ca.* 20 °C in ether (500 ml)	Cryst. from Et_2O–pentane (1 : 1)	$[Cl_2P(S)]_2NPh$ (mixed with $PSCl_3$)	12	64—65

The ^1H and ^{31}P n.m.r. data for the phosphinothioyl-derivatives and cyclodiphosphazanes is given in Table 1. The low-field ^1H shifts of the *N*-methyl and *N*-methylene signals are, in part, a reflection of the weakly basic nature of the bridging nitrogen atoms. These ^1H shifts may be compared with those for the *N*-methyl signals in $Cl_2P(S){\cdot}NHMe$ (Table 1) and in $Cl_2P(S){\cdot}NMe_2$ (τ 6·98 [21]). The relative magnitudes of the spin–spin coupling constants between the *N*-alkyl protons and the phosphorus atoms follows the expected [1,22] order: $J_{P(S)\text{-}N\text{-}C\text{-}H} > J_{P(O)\text{-}N\text{-}C\text{-}H} \gg J_{P^{III}\text{-}N\text{-}C\text{-}H}$. It is interesting to note that the coupling constants $J_{P\text{-}N\text{-}P}$ are increased when an *N*-alkyl-group is replaced by an *N*-phenyl-group, the reverse of the trend observed for *P–N–P* coupling in derivatives of the type $(F_2P)_2NR$ (R = alkyl, aryl).[23]

The i.r. absorptions associated with the stretching vibrations of the $P{-}\overset{C}{\overset{|}{N}}{-}P$ skeleton can readily be assigned in the *N*-alkyl-derivatives (Table 2). However, the spectra of the *N*-phenyl compounds leave some ambiguity as to the nature of the bands in the region 1000—800 cm^{-1}. Similarly, the bands associated with the P–S vibration are not easily assigned, except in the case of $[Cl_2P(S)]_2NMe$. The P^V–N and P^{III}–N bands do not appear to give separate absorptions in the 900 cm^{-1} region for derivatives of the type $Cl_2P(S){\cdot}NR{\cdot}PCl_2$, so that these vibrations are presumably strongly coupled. As found in the dichlorophosphinyl-derivatives [1] ν_{as}(P–N–P) increases on passing from P^{III}–N–P^{III} to P^V–N–P^{III} to P^V–N–P^V compounds.

EXPERIMENTAL

Solvents were dried by conventional means. Phosphorus trichloride, phosphoryl(V) chloride, and thiophosphoryl(V) chloride were purified by distillation. Dichlorophosphinothioylamines $Cl_2P(S){\cdot}NHR$ (R = Me [16] and Ph [15]), and bis(dichlorophosphino)amines $(Cl_2P)_2NR$ (R = Me,[8] Et,[8] and Ph [9]) were prepared by literature methods. Hydrogen chloride gas was dried by passage through a column of phosphorus pentoxide. All reactions were carried out under a flush of dry nitrogen. ^1H and ^{31}P Spectra were measured on a Perkin-Elmer R10 spectrometer at 60 and 24·3 MHz respectively. The ^{31}P spectra were obtained from

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samples contained in 8·5 mm o.d. non-spinning tubes and 85% H_3PO_4 was used as an external standard. I.r. spectra were recorded on Perkin-Elmer 225 or 457 spectrometers. Mass spectra were obtained from an A.E.I. MS12 spectrometer. Examples of the preparative methods are given in detail below. The remaining methods are summarised in Table 3, and analytical data is given in Table 4.

Dichlorophosphinothioyl(dichlorophosphino)methylamine.— Bis(dichlorophosphino)methylamine (12·4 g, 0·53 mol), sulphur (1·7 g, 0·53 mol) and finely ground anhydrous aluminium chloride (*ca.* 0·5 g) were heated to *ca.* 150°, when a strongly exothermic reaction occurred. The heat source was removed and the mixture was stirred (30 min). Distillation of the resultant yellow oil under reduced pressure gave dichlorophosphinothioyl(dichlorophosphino)-methylamine (12·1 g, 86%), b.p. 55—60 °C/0·1 mmHg, with i.r., ^1H and ^{31}P n.m.r. identical to that reported.[1] This product was never obtained completely free of traces (<3%, ^1H n.m.r.) of 1,3-dimethyl-2,4-dichloro-2,4-dithiocyclodiphosphazanes (see below).

TABLE 4

Analytical data

Compound	Found C	Found H	Found Cl	Found m/e *	Calculated C	Calculated H	Calculated Cl	Calculated m/e *
$[Cl_2P(S)]_2NMe$	4·1	1·1	47·6	295	4·0	1·0	47·8	295
$Cl_2P(S)NEtPCl_2$	8·5	1·8	51·3		8·6	1·8	50·9	
$[Cl_2P(S)]_2NEt$	8·0	2·0	45·5	309	7·7	1·6	45·7	309
$[Cl_2P(S)]_2NPh$	20·5	1·5	39·3	357	20·1	1·4	39·6	357
$Cl_2P(S)NPhP(O)Cl_2$	21·2	1·4	40·6	341	21·0	1·5	41·4	341
$[ClP(S)NEt]_2$	17·5	3·7	24·8		17·0	3·5	25·1	

* For ^{35}Cl containing ions.

Bis(dichlorophosphinothioyl)methylamine.— Bis(dichlorophosphino)methylamine (14·6 g, 0·063 mol) and sulphur (4·1 g, 0·128 mol) were heated together in the presence of anhydrous aluminium chloride (*ca.* 0·5 g) as described above; the resultant yellow oil was distilled under reduced pressure to give *bis(dichlorophosphinothioyl)methylamine* (16·9 g, 91%), b.p. 84—85 °C/0·5 mmHg, m.p. 61—62 °C. Alternatively, purification could be achieved by crystallisation of the oil from light petroleum, b.p. 60—80 °C.

Pyrolysis of Dichlorophosphinothioyl(dichlorophosphino)-methylamine.— Dichlorophosphinothioyl(dichlorophosphino)methylamine (14·0 g, 0·053 mol) was heated at 200—250 °C, when phosphorus trichloride (7·1 g, 98%) was evolved; it was identified by its b.p. (76 °C) and ^{31}P n.m.r. spectrum (−219 p.p.m.). The oily residue was distilled under reduced pressure to give a colourless oil, b.p. 70—80 °C/0·1 mmHg, and a white solid which sublimed out of the distillation flask at the same pressure. The solid was recrystallised from light petroleum (b.p. 40—60°) to give 1,3-dimethyl-2,4-dichloro-2,4-dithioxocyclodiphosphazane (1·8 g, 24%), m.p. 115—135 °C, ^{31}P shift −52 p.p.m. as a mixture of geometrical isomers (previously reported[13] m.p. 120—122 °C, ^{31}P shift −51·5 p.p.m.). The oil contained a mixture of products of which only the cyclodiphosphazane (above) was identifiable (^1H and ^{31}P n.m.r.).

Dichlorophosphinyl(dichlorophosphinothioyl)aniline.— Triethylamine (2·6 g, 0·026 mol) was added slowly to a well stirred mixture of dichlorophosphinothioylaniline (5·9 g, 0·026 mol) and phosphoryl chloride (4·0 g, 0·026 mol) in diethyl ether (100 ml) at ambient temperature. Stirring was continued for 1 h, when the precipitate was removed and the ether evaporated from the filtrate. The residue was recrystallised from a mixture of diethyl ether and n-pentane (1 : 1) to give *dichlorophosphinyl(dichlorophosphinothioyl)aniline* (6·1 g, 68%), m.p. 80—81°. Reactivity to hydrogen chloride was investigated by passing the gas through a solution of the appropriate phosphinothioyl- or dithiocyclodiphosphazane-derivative in methylene chloride at ambient temperatures for *ca.* 1 h.

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