Nuclear Magnetic Resonance Spectroscopic Characterisation and the Crystal and Molecular Structures of $Ph_3PS{\cdot}AlCl_3$ and $Ph_3PSe{\cdot}AlCl_3$: A Classification of the Co-ordinative Bonding Modes of the Phosphine Chalcogenides §

Neil Burford,*† Bruce W. Royan, and Rupert E. v. H. Spence
Department of Chemistry, Dalhousie University, Halifax, Nova Scotia, B3H 4J3, Canada
Robin D. Rogers*‡
Department of Chemistry, Northern Illinois University, DeKalb, Illinois 60115, U.S.A.

A series of compounds with the general formula $R_3PE{\cdot}AlCl_3$ (R = Ph or NMe_2, E = S or Se) has been examined by n.m.r. spectroscopy as a contribution toward the characterisation of the P–E bond and of the co-ordinate bond. Two derivatives, $Ph_3PS{\cdot}AlCl_3$ and $Ph_3PSe{\cdot}AlCl_3$, have been studied by *X*-ray crystallography. [Crystal data: $C_{18}H_{15}AlCl_3PS$, monoclinic, space group, $P2_1/n$, $a = 9.710(2)$, $b = 9.464(1)$, $c = 21.893(5)$ Å, $\beta = 95.15(2)°$, $Z = 4$, $R = 0.042$; $C_{18}H_{15}AlCl_3PSe$, triclinic, space group, $P\bar{1}$, $a = 8.967(2)$, $b = 12.626(4)$, $c = 18.242(4)$ Å, $\alpha = 84.83(2)$, $\beta = 89.02(2)$, $\gamma = 85.67(2)°$, $Z = 4$, $R = 0.044$.] In contrast to the oxygen analogues, the sulphur and selenium derivatives exhibit bent geometries [P–S–Al 109.62(8), P–Se–Al (mean) = 107.0(1)°]. The structures are maintained in solution, as demonstrated by the ^{27}Al n.m.r. spectra. The ^{31}P and ^{13}C n.m.r. spectra are informative of the changes associated with adduct formation, and show the oxygen derivatives (E = O) to be unique. Disruption of the P–E π interaction due to adduct formation is more dramatic for the sulphur and selenium than for the oxygen derivatives. The extensive information available in the literature is re-evaluated in the light of the present results, and a classification for the co-ordinative bonding modes of the phosphine chalcogenides is proposed.

Spectroscopic and structural studies on complexes of phosphine chalcogenides (R_3PE; E = O, S, or Se) have played an important role in the development of a model for the phosphoryl bond.[1] Nevertheless, the phosphoryl systems continue to attract attention and the nature of the P–E bond is a point of much discussion by theoreticians[2] and experimentalists.[3–5] We have recently discovered that aluminium halide ($AlCl_3$ and $AlBr_3$) adducts of phosphine oxides adopt a rare linear P–O–Al geometry in both the solid state and in solution.[6] Here we report a comparative investigation of the sulphide and selenide analogues and show them to be severely bent in the solid state. Moreover, the n.m.r. data are consistent with a bent structure in solution. The unique behaviour of the phosphine oxides is supported by extensive information available in the literature,[6] and is further emphasised by the new data, culminating in a proposal for a classification of complexes of the type $R_3PE{\cdot}M$ (M = Lewis acid, *e.g.* $AlCl_3$, BF_3, or transition-metal complex).

Experimental

General Procedures.—The compounds Ph_3PS (Pflatz and Bauer) and Ph_3PSe (Aldrich) were obtained commercially and used without purification; $(Me_2N)_3PS$ was prepared by reaction of $(Me_2N)_3P$ with S_8 in Et_2O at 0 °C. Anhydrous aluminium chloride (Aldrich) was sublimed under vacuum. Dichloromethane was dried over P_2O_5 and CaH_2, carbon disulphide over CaH_2, and these were stored in evacuated bulbs. Solids were manipulated in a Vacuum/Atmospheres nitrogen-filled glove-box. Infrared spectra were recorded as Nujol mulls on CsI plates using a Perkin-Elmer 283B spectrophotometer and n.m.r. spectra on a Nicolet NT-360 spectrometer in CH_2Cl_2. Chemical shifts are reported in p.p.m. relative to external standards {85% H_3PO_4 for ^{31}P, $[Al(H_2O)_6]^{3+}$ for ^{27}Al; ^{77}Se signals were externally referenced initially to selenous acid and then re-referenced to $SeMe_2$} and relative to the internal CH_2Cl_2 signal for ^{13}C spectra. Glass equipment was flame dried before use. Reactions involved mixing a CH_2Cl_2 solution of the phosphine chalcogenide with a solution/suspension of $AlCl_3$ in an evacuated (10^{-3} Torr) dual-compartment vessel. Products were isolated as crystalline solids by removal of the solvent *in vacuo*. All complexes were air sensitive. N.m.r. spectra were obtained on samples (10-mm flame-sealed Pyrex tubes), which were prepared at approximate concentrations of 0.018 and 0.058 mol dm^{-3} for $Ph_3PS{\cdot}AlCl_3$, 0.018 and 0.071 mol dm^{-3} for $Ph_3PSe{\cdot}AlCl_3$, and 0.02 and 0.10 mol dm^{-3} for $(Me_2N)_3PS{\cdot}AlCl_3$ in CH_2Cl_2. The n.m.r. data are presented in Table 1 together with data for related compounds.

Characterisation data.—$(Me_2N)_3PS{\cdot}AlCl_3$: 1 295m, 1 165m, 1 060w, 970s, 745s, 675m, 540m, 490vs, 435vs, 385w, and 345w cm^{-1}, m.p. 75—77 °C.

$Ph_3PSe{\cdot}AlCl_3$: 1 100s, 1 000w, 745s, 720s, 685s, 545vs, 510vs, 495vs, 450w, 395s, and 280w cm^{-1}, m.p. 107—109 °C.

$Ph_3PS{\cdot}AlCl_3$: m.p. 137—140 °C.

Of principal interest are the P–Se stretches, which we have assigned to the peak at 545 cm^{-1} by comparison with the similar bands in the spectra of $Ph_3PSe{\cdot}HgX_2$ (X = Cl, 543; Br, 542; I, 542 cm^{-1}).[7] The bands at 435 for $(Me_2N)_3PS{\cdot}AlCl_3$ and 395 cm^{-1} for $Ph_3PSe{\cdot}AlCl_3$ are assigned to the Al–Cl stretch.

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† Author for correspondence on chemical aspects.

‡ Author for correspondence on crystallography.

§ Triphenylphosphine sulphide–aluminium trichloride (1/1) and triphenylphosphine selenide–aluminium trichloride (1/1).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix—xxii.

Non-S.I. unit employed: Torr ≈ 133 Pa.

Table 1. Carbon-13, ^{31}P, ^{27}Al, and ^{77}Se n.m.r. data[a] for derivatives of R_3PE and $R_3PE{\cdot}AlCl_3$ and related compounds

	^{13}C[b]					
	ipso	*ortho*	*meta*	*para*	^{31}P	^{27}Al[c]
Ph_3PO	132.8 (103.5)	132.1 (9.8)	128.5 (17.7)	131.8 (2.4)	29.3	
Ph_3PS	133.0 (85.0)	132.2 (10.6)	128.5 (12.7)	131.5 (2.8)	43.2	
Ph_3PSe[d]	131.9 (70.8)	132.7 (9.8)	128.5 (12.2)	131.5 (3.7)	35.8	
$Ph_3PO{\cdot}AlCl_3$	124.7 (109.4)	132.5 (12.2)	129.3 (12.6)	134.5	44.9	90 (40)
$Ph_3PO{\cdot}AlBr_3$	124.1 (109.8)	132.8 (11.8)	129.5 (13.6)	134.8	45.7	79 (31)
$Ph_3PS{\cdot}AlCl_3$	124.4 (81.7)	133.2 (10.9)	129.4 (13.3)	134.1	42.8	107 (200) 102 (<20)
$Ph_3PSe{\cdot}AlCl_3$[d]	124.1 (79.7)	133.5 (10.2)	129.5 (13.2)	134.0	33.7	106 (200) 102 (<20)
Ph_3POH^+[e]	120.0 (107.4)	131.1 (9.8)	129.0 (12.2)	132.8	57.2	
Ph_3PSH^+[e]	119.3 (85.4)	132.6 (11.8)	129.8 (14.6)	135.2	42.6	
Ph_3PSeH^+[d,e]	116	130.8	133.8	137.0	37.6	
$(Me_2N)_3PO$					22.0—25.6[f]	
$(Me_2N)_3PS$					81.4, 81.7[f]	
$(Me_2N)_3PO{\cdot}AlCl_3$		36.4			24.4	88 (18)
$(Me_2N)_3PS{\cdot}AlCl_3$					68.6	107 (80) 102 (<20)

[a] Chemical shift in p.p.m. [b] Coupling constants J_{PC}/Hz in parentheses. [c] $\Delta\nu_{\frac{1}{2}}$/Hz values in parentheses. [d] Selenium-77 n.m.r. data δ/p.p.m. (J_{PSe}/Hz in parentheses); Ph_3PSe, −275 (730); $Ph_3PSe{\cdot}AlCl_3$ −190 (540), Ph_3PSeH^+ — (414). Selenium-77 n.m.r. data for examples of related compounds: $Bu^n{}_3PSe$, −384(689); Me_3PSe, −235(684); $[Cd(Ph_3PSe)_3]^{2+}$—(542); $[Cd(Ph_3PSe)_4]^{2+}$—(585); $[HgX_2(Bu_3PSe)_2]$X = Cl, −284(512,522); Br, −280 (542, 531); I, −276 (562, 548); $[Hg(SCN)_2(Bu_3PSe)_2]$, −289 (527) (I. J. Colquhoun and W. McFarlane, *J. Chem. Soc., Dalton Trans.*, 1981, 658; P. A. W. Dean and L. Polensek, *Can. J. Chem.*, 1980, **58**, 1627; R. Colton and D. Dakternieks, *Aust. J. Chem.*, 1980, **33**, 1463); Me_2PSeMe, 58 (205); $Me_2P(S)SeMe$, 196 (341);[13] $[\{(Et_2N)_2PSe\}_2]^{2+}$ — (360).[14] [e] In H_2SO_4. [f] M. M. Crutchfield, C. H. Dungan, J. H. Letcher, V. Mark, and J. R. Van Wazer, *Top. Phosphorus Chem.*, 1967, **5**, 227.

X-Ray Data Collection, Solution, and Refinement.—Crystals of $Ph_3PS{\cdot}AlCl_3$ and $Ph_3PSe{\cdot}AlCl_3$ suitable for crystallography were obtained from saturated solutions of CH_2Cl_2–CS_2 (1:1) by cooling to 0 °C for 1 week. Transparent crystals were selected in the dry-box and mounted in thin-walled Pyrex capillaries under nitrogen. An Enraf-Nonius CAD-4 diffractometer was used to determine the cell dimensions and to collect the data. The crystal data and data-collection parameters are presented in Table 2. The unit-cell constants were obtained by least-squares analysis of the diffractometer settings for 25 well centred reflections for which $\theta > 19°$. Scattering factors for neutral atoms were corrected for anomalous dispersion.[8] The structures were solved by direct methods (MULTAN)[9] and refined by a full-matrix least squares procedure[10] using anisotropic thermal parameters for all non-hydrogen atoms.

$Ph_3PS{\cdot}AlCl_3$. The space group was determined to be the centric $P2_1/n$ from the observation of systematic absences. Least-squares refinement with isotropic thermal parameters led to $R = 0.096$. The hydrogen atoms were placed in calculated positions 0.95 Å from the bonded carbon atom and allowed to ride on that atom with B fixed at 5.5 Å^2. Final refinement involved all non-hydrogen atoms.

$Ph_3PSe{\cdot}AlCl_3$. The space group was determined to be either centric $P\bar{1}$ or acentric $P1$. Statistical tests indicated the former. Subsequent solution and successful refinement of the structure confirmed this. Least-squares refinement with isotropic thermal parameters led to $R = 0.085$. The hydrogen atoms were placed in calculated positions 0.95 Å from the bonded carbon atom and allowed to ride on that atom with B fixed at 5.5 Å^2. Final refinement involved anisotropic thermal parameters for all non-hydrogen atoms.

The final fractional atomic co-ordinates for $Ph_3PS{\cdot}AlCl_3$ and $Ph_3PSe{\cdot}AlCl_3$ are given in Tables 3 and 4, respectively. Selected bond distances and angles are provided in Table 5. Views of the molecules are given in Figures 1 and 2, respectively.[11]

Additional material available from the Cambridge Crystallographic Data centre comprises H-atom co-ordinates, thermal parameters, and remaining bond lengths and angles.

Results and Discussion

It is generally understood that the adduct bond between a phosphine chalcogenide and a Lewis acid is formed at the expense of the phosphorus–chalcogen π bond of the free base.[1] This conclusion is the result of extensive i.r. spectroscopic studies and a large number of X-ray crystal structures (Table 6, see also Table 7 in ref. 6). While our studies confirm and

Table 2. Experimental data for the crystallographic analyses[a]

	$Ph_3PS{\cdot}AlCl_3$	$Ph_3PSe{\cdot}AlCl_3$
Formula	$C_{18}H_{15}AlCl_3PS$	$C_{18}H_{15}AlCl_3PSe$
M	427.70	474.59
Crystal class	Monoclinic	Triclinic
Space group	$P2_1/n$	$P\bar{1}$
a/Å	9.710(2)	8.967(2)
b/Å	9.464(1)	12.626(4)
c/Å	21.893(5)	18.242(4)
α/°	—	84.83(2)
β/°	95.15(2)	89.02(2)
γ/°	—	85.67(2)
U/Å^3	2 004	2 051
D_c/g cm^{-3}	1.42	1.54
μ/cm^{-1}	6.17	22.4
Crystal dimensions/mm	0.25 × 0.25 × 0.25	0.15 × 0.30 × 0.15
$F(000)$	872	944
Standard reflections	6, 0, 0; 0, 4, 0; 0, 0, 16	3, 0, 0; 0, 5, 0; 0, 0, 10
Decay	±1%	±2%
Range of h, k, l	+11, +11, ±26	+10, ±15, ±21
Reflections measured	3 959	7 187
Unique reflections observed $[F_o > 5\sigma(F_o)]$	1 835	3 665
No. of parameters varied	217	424
Weights w	$[\sigma(F_o)^2 + 0.0002\,F_o^2]^{-1}$	$[\sigma(F_o)^2 + 0.00015\,F_o^2]^{-1}$
$S^b = [\Sigma(w)\lVert F_o\rvert - \lvert F_c\rVert)^2/(N - P)]^{\frac{1}{2}}$	0.77	0.80
$R = \Sigma\lVert F_o\rvert - \lvert F_c\rVert/\Sigma\lvert F_o\rvert$	0.042	0.044
$R' = [\Sigma w(\lVert F_o\rvert - \lvert F_c\rVert)^2/\Sigma(w\lvert F_o\rvert)^2]^{\frac{1}{2}}$	0.043	0.044
$\Delta\rho$/e Å^{-3}	0.3	0.4

[a] Details in common, $Z = 4$, Enraf Nonius CAD-4 diffractometer; Mo-K_α radiation (graphite monochromated) ($\lambda = 0.710\ 73$ Å). Scan mode ω—2θ, $2 < 2\theta < 50°$ width 0.80/0.35 tan θ. [b] P = Number of parameters, N = number of variables.

Table 3. Final fractional co-ordinates for $Ph_3PS{\cdot}AlCl_3$ with estimated standard deviations (e.s.d.s) in parentheses

Atom	X/a	Y/b	Z/c
Cl(1)	1.392 5(2)	0.067 6(2)	0.650 95(8)
Cl(2)	1.424 1(2)	0.431 7(2)	0.625 51(7)
Cl(3)	1.228 9(2)	0.218 0(2)	0.518 46(7)
S	1.120 5(1)	0.325 2(1)	0.667 22(7)
P	0.965 5(1)	0.180 9(1)	0.660 09(6)
Al	1.297 0(2)	0.250 3(2)	0.611 90(7)
C(1)	0.884 7(5)	0.187 7(5)	0.730 9(2)
C(2)	0.944 9(6)	0.255 3(6)	0.782 4(2)
C(3)	0.879 1(6)	0.256 9(6)	0.836 1(2)
C(4)	0.755 2(7)	0.191 6(6)	0.838 5(3)
C(5)	0.693 5(7)	0.123 2(7)	0.788 0(3)
C(6)	0.758 7(6)	0.120 8(7)	0.734 5(3)
C(7)	0.839 9(5)	0.225 6(5)	0.597 9(2)
C(8)	0.831 0(6)	0.361 9(6)	0.575 0(2)
C(9)	0.728 4(7)	0.398 0(6)	0.529 4(3)
C(10)	0.635 6(7)	0.299 7(7)	0.506 6(3)
C(11)	0.642 2(6)	0.164 9(7)	0.528 1(3)
C(12)	0.743 7(5)	0.126 2(6)	0.573 4(2)
C(13)	1.023 7(5)	0.003 7(5)	0.649 1(2)
C(14)	1.068 1(5)	−0.078 5(6)	0.699 4(2)
C(15)	1.122 9(6)	−0.210 6(6)	0.690 1(3)
C(16)	1.133 5(6)	−0.261 3(6)	0.632 1(3)
C(17)	1.089 2(6)	−0.180 5(6)	0.582 4(3)
C(18)	1.033 7(5)	−0.048 0(5)	0.590 4(2)

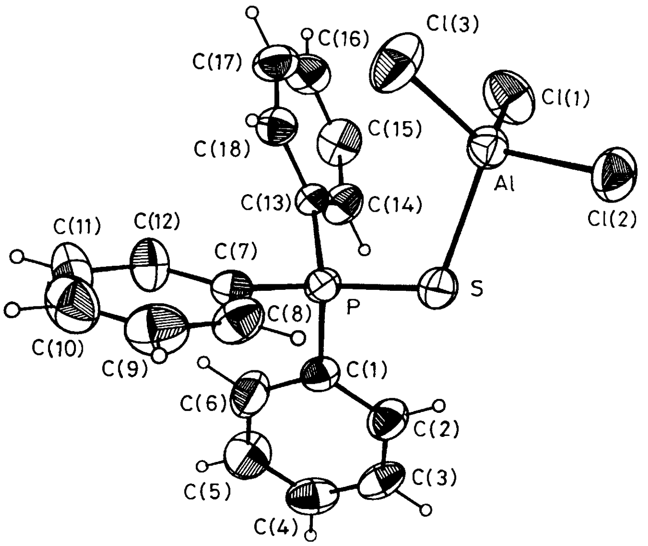

Figure 1. A view of $Ph_3PS{\cdot}AlCl_3$

support this model, we are aware of anomalous behaviour for the oxide derivatives and have recently discovered extreme examples.[6] The compounds $Ph_3PO{\cdot}AlCl_3$ and $Ph_3PO{\cdot}AlBr_3$ both adopt a linear geometry in the solid state (space group $R\bar{3}$, P–O–Al 180°). Sharp signals ($\Delta\nu_{\frac{1}{2}}$40 and 31 Hz, respectively) are observed in the ^{27}Al n.m.r. spectra of these compounds and a sharper line ($\Delta\nu_{\frac{1}{2}}$18 Hz) is observed for $(Me_2N)_3PO{\cdot}AlCl_3$,[6] indicating that linear geometry is maintained in solution.[12] To confirm the anomaly and define these systems more accurately, we have examined phosphine sulphide and phosphine selenide derivatives.

N.M.R. Spectroscopic Data.—The ^{31}P and ^{13}C n.m.r. data (Table 1) provide a useful insight into the electronic structure of the phosphine chalcogenides and the corresponding adducts. The adduct interaction effects a significant deshielding of the ^{31}P chemical shifts for the phosphine oxides. This is most pronounced in the conjugate acid Ph_3POH^+.[3] In contrast, chemical shifts for the adducts of the phosphine sulphides and selenides are independent of the nature of the acid, and are

Table 4. Final fractional co-ordinates for $Ph_3PSe{\cdot}AlCl_3$ with e.s.d.s in parentheses

Atom	*X/a*	*Y/b*	*Z/c*	Atom	*X/a*	*Y/b*	*Z/c*
Se(1)	0.694 93(9)	0.125 51(6)	0.234 07(4)	Se(2)	0.334 60(9)	0.393 13(6)	0.249 95(4)
Cl(1)	0.544 0(2)	−0.130 3(2)	0.181 9(1)	Cl(4)	0.248 1(3)	0.678 1(2)	0.293 8(1)
Cl(2)	0.658 7(3)	0.066 8(2)	0.050 9(1)	Cl(5)	0.444 7(3)	0.479 2(2)	0.409 5(1)
Cl(3)	0.927 6(2)	−0.092 3(2)	0.156 3(1)	Cl(6)	0.058 9(3)	0.485 6(2)	0.396 2(1)
P(1)	0.610 4(2)	0.062 1(1)	0.340 7(1)	P(2)	0.186 1(2)	0.428 8(1)	0.156 0(1)
Al(1)	0.707 0(2)	−0.020 4(2)	0.153 6(1)	Al(2)	0.259 1(3)	0.518 0(2)	0.339 3(1)
C(1)	0.698 5(7)	0.130 5(5)	0.408 8(4)	C(19)	0.157 5(8)	0.306 5(5)	0.117 7(4)
C(2)	0.693 3(8)	0.241 3(5)	0.402 3(4)	C(20)	0.266 3(8)	0.221 0(5)	0.122 8(4)
C(3)	0.764 6(9)	0.295 0(6)	0.451 4(5)	C(21)	0.247(1)	0.131 4(6)	0.087 4(5)
C(4)	0.837 9(9)	0.239 5(7)	0.510 2(4)	C(22)	0.116 8(9)	0.124 9(6)	0.049 8(5)
C(5)	0.843 7(8)	0.130 2(7)	0.517 9(4)	C(23)	0.008 8(9)	0.207 1(7)	0.043 9(5)
C(6)	0.772 1(8)	0.074 5(6)	0.468 8(4)	C(24)	0.0294 (9)	0.297 4(6)	0.079 0(5)
C(7)	0.410 0(7)	0.091 7(5)	0.347 6(4)	C(25)	0.004 5(7)	0.487 7(5)	0.180 8(3)
C(8)	0.317 5(9)	0.058 0(6)	0.296 3(4)	C(26)	−0.087 6(9)	0.429 1(6)	0.227 4(4)
C(9)	0.165 4(9)	0.084 5(7)	0.299 1(5)	C(27)	−0.224(1)	0.472 7(8)	0.246 5(5)
C(10)	0.106 0(9)	0.144 7(7)	0.350 5(5)	C(28)	−0.273 4(9)	0.573 1(7)	0.220 2(5)
C(11)	0.195 5(9)	0.179 3(6)	0.402 4(5)	C(29)	−0.182 1(9)	0.630 5(6)	0.174 2(5)
C(12)	0.349 2(8)	0.153 4(6)	0.400 1(4)	C(30)	−0.042 2(8)	0.588 6(6)	0.154 5(5)
C(13)	0.654 2(7)	−0.078 5(5)	0.360 1(4)	C(31)	0.268 0(7)	0.514 8(5)	0.086 4(4)
C(14)	0.548 7(8)	−0.142 6(6)	0.394 5(4)	C(32)	0.270 7(8)	0.493 0(6)	0.012 6(4)
C(15)	0.585(1)	−0.250 4(6)	0.412 7(4)	C(33)	0.330 6(8)	0.560 0(6)	−0.042 1(4)
C(16)	0.726(1)	−0.293 7(6)	0.395 6(4)	C(34)	0.389 5(9)	0.649 8(7)	−0.023 0(5)
C(17)	0.831 0(9)	−0.231 4(6)	0.362 2(4)	C(35)	0.391 7(9)	0.674 5(6)	0.048 3(5)
C(18)	0.796 8(8)	−0.123 1(5)	0.344 5(4)	C(36)	0.331 9(8)	0.606 3(6)	0.103 0(4)

Table 5. Selected bond distances (Å) and angles (°) with e.s.d.s in parentheses

$Ph_3PS{\cdot}AlCl_3$		$Ph_3PSe{\cdot}AlCl_3$			
P–S	2.028(2)	P(1)–Se(1)	2.182(2)	P(2)–Se(2)	2.181(2)
S–Al	2.297(2)	Se(1)–Al(1)	2.452(2)	Se(2)–Al(2)	2.421(2)
P–C(1)	1.801(5)	P(1)–C(1)	1.800(7)	P(2)–C(19)	1.789(7)
P–C(7)	1.795(5)	P(1)–C(7)	1.812(6)	P(2)–C(25)	1.807(6)
P–C(13)	1.793(5)	P(1)–C(13)	1.793(7)	P(2)–C(31)	1.781(7)
Al–Cl(1)	2.107(2)	Al(1)–Cl(1)	2.117(3)	Al(2)–Cl(4)	2.111(3)
Al–Cl(2)	2.120(2)	Al(1)–Cl(2)	2.119(3)	Al(2)–Cl(5)	2.118(3)
Al–Cl(3)	2.115(2)	Al(1)–Cl(3)	2.113(3)	Al(2)–Cl(6)	2.106(3)
P–S–Al	109.62(8)	P(1)–Se(1)–Al(1)	106.95(7)	P(2)–Se(2)–Al(2)	107.15(7)
Cl(1)–Al–Cl(2)	112.2(1)	Cl(1)–Al(1)–Cl(2)	111.0(1)	Cl(4)–Al(2)–Cl(5)	112.5(1)
Cl(1)–Al–Cl(3)	111.2(1)	Cl(1)–Al(1)–Cl(3)	113.0(1)	Cl(4)–Al(2)–Cl(6)	110.2(1)
Cl(2)–Al–Cl(3)	112.37(9)	Cl(2)–Al(1)–Cl(3)	111.8(1)	Cl(5)–Al(2)–Cl(6)	110.3(1)
Cl(1)–Al–S	111.17(9)	Cl(1)–Al(1)–Se(1)	112.3(1)	Cl(4)–Al(2)–Se(2)	112.7(1)
Cl(2)–Al–S	97.42(8)	Cl(2)–Al(1)–Se(1)	100.2(1)	Cl(5)–Al(2)–Se(2)	96.2(1)
Cl(3)–Al–S	111.80(9)	Cl(3)–Al(1)–Se(1)	107.9(1)	Cl(6)–Al(2)–Se(2)	114.3(1)
S–P–C(1)	106.7(2)	Se(1)–P(1)–C(1)	106.3(2)	Se(2)–P(2)–C(19)	108.3(2)
S–P–C(7)	110.4(2)	Se(1)–P(1)–C(7)	110.5(2)	Se(2)–P(2)–C(25)	113.0(2)
S–P–C(13)	113.5(2)	Se(1)–P(1)–C(13)	113.5(2)	Se(2)–P(2)–C(31)	111.0(2)
C(1)–P–C(7)	109.0(2)	C(1)–P(1)–C(7)	108.2(3)	C(19)–P(2)–C(25)	107.3(3)
C(7)–P–C(13)	108.6(2)	C(7)–P(1)–C(13)	109.7(3)	C(25)–P(2)–C(31)	109.1(3)
C(1)–P–C(13)	108.4(2)	C(1)–P(1)–C(13)	108.5(3)	C(19)–P(2)–C(31)	107.9(3)

similar to those of the corresponding free bases, as recognised by Glidewell and Leslie.[4] The ^{13}C chemical shifts for the carbon nuclei of the phenyl groups are uniformly sensitive to chemical changes at the chalcogen position for all chalcogenides. While the *ortho* and *meta* positions show no significant differences for all derivatives, the *ipso* position shows an increased shielding upon adduct formation with $AlCl_3$ and H^+, and (to a lesser extent) the *para* positions are deshielded.[3] Such effects can be rationalised in terms of simple resonance considerations, and provide evidence for π interaction between the phenyl groups and the phosphorus centre.[3] We conclude that co-ordination of the phosphine oxides effects a perturbation of both the σ and π frameworks of the free base, while the sulphide and selenide derivatives experience principally π disruption, resulting in a negligible change at the phosphorus centre, but a significant influence at the *ipso* carbon centres. The additional probe available in the selenium derivatives offers further information. Selenium-77 n.m.r. data were obtained on a saturated solution of $Ph_3PSe{\cdot}AlCl_3$. The ^{77}Se chemical shift is significantly deshielded from that of Ph_3PSe[13] (Table 1) consistent with donation from the selenium centre. Nevertheless, J_{PSe} for $Ph_3PSe{\cdot}AlCl_3$ is intermediate between that of Ph_3PSe and those of systems containing representative single P–Se bonds.[13,14] We conclude that a degree of π bonding is maintained in the $AlCl_3$ complex. Disruption of the π framework is more pronounced in the conjugate acid Ph_3PSeH^+, however J_{PSe}[4] is significantly greater than that for the single-bonded systems.[13,14]

The ^{27}Al n.m.r. spectra of sulphide and selenide derivatives show a broad resonance (200 Hz) centred at 107 p.p.m. and a sharp signal at 102 p.p.m. corresponding to $AlCl_4^-$.[12] Representative spectra are shown in Figure 3 and are diagnostic

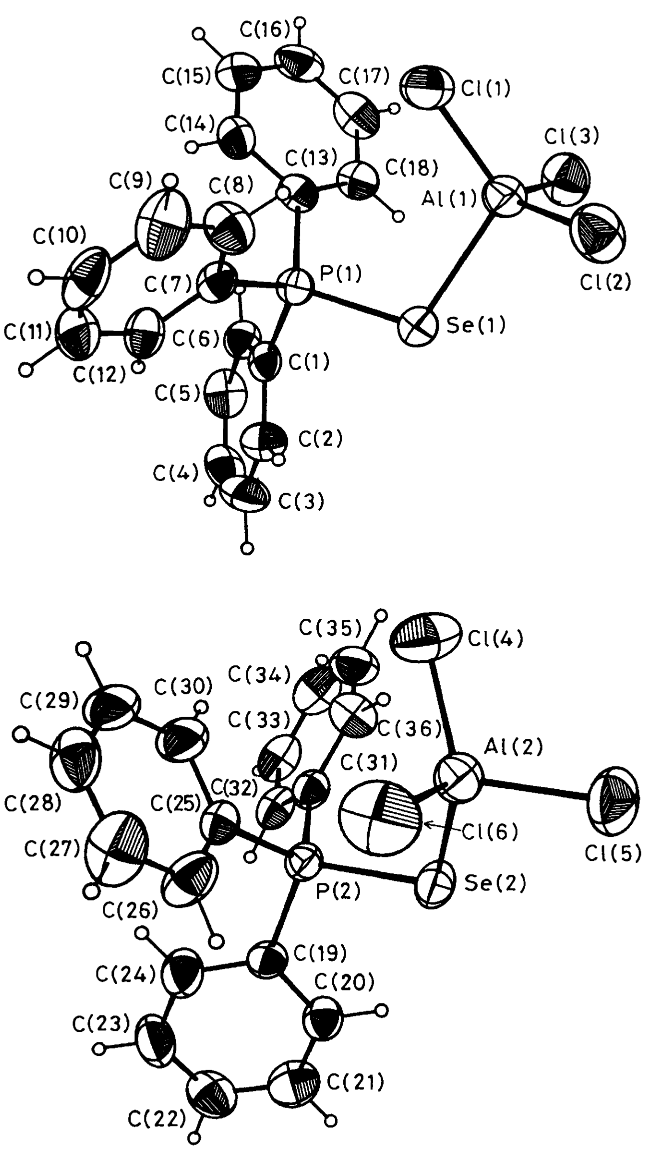

Figure 2. A view of the two molecules of $Ph_3PSe{\cdot}AlCl_3$

for these adducts.[14] We assign the broad signal to the complex, in view of the bent structures observed in the solid state (see above). The integration ratios range from 5:1 to 10:1 and appear to be concentration dependent, the ratio of $AlCl_4^-$ increasing with increasing dilution, as illustrated for $(Me_2N)_3PS{\cdot}AlCl_3$ in Figure 3. Interestingly, for the phenyl derivatives dilute samples (0.018 mol dm^{-3}) also show a significant presence of free base in the ^{31}P n.m.r. spectra. We conclude that the sulphide and selenide complexes are labile and dissociate in solution. Consistently, the mass spectra of these complexes show no molecular ion. The highest-mass peaks correspond to the free bases. While the mechanism of formation of small amounts of $AlCl_4^-$ in solution is unclear, the free $AlCl_3$ resulting from dissociation is probably the origin. The lability of these adducts is further demonstrated by their slow decay in CH_2Cl_2 and relatively fast reaction with tetrahydrofuran (thf). Solutions in thf show a single ^{27}Al n.m.r. signal at 63 p.p.m. ($\Delta\nu_{\frac{1}{2}}$ = 300 Hz), which corresponds to the adduct $AlCl_3(thf)_2$.[15] Dilute solutions of the phosphine oxide complexes show no indication of free base in the ^{31}P n.m.r. spectra, nor the presence of $AlCl_4^-$ in the ^{27}Al n.m.r. spectra.[6]

Table 6. Comparison of structural features for some phosphine chalcogenide (E = S or Se) complexes

	P–E (Å)	P–E–M (°)	Ref.
Ph_3PS	1.950(3)		16
$Ph_3PS{\cdot}AlCl_3$	2.028(2)	109.62(8)	
$2Ph_3PS{\cdot}3I_2$	2.007(3)	107.0(1)	*a*
$Ph_3PS{\cdot}MoOCl_3$	2.041(1)	111.31(4)	*b*
$Ph_3PS{\cdot}NbSCl_3$	2.028(5)	116.6(2)	*c*
	2.026(6)	111.5(2)	
$[Cu\{Ph_2P(S)CH_2P(S)Ph_2\}Cl]$	1.970(2)	91.52(8)	*d*
	1.974(3)	95.68(8)	
$[\{Cu(Me_3PS)Cl\}_3]$	2.024(2)	104.72(5)	*e*
	2.026(1)	103.88(6)	
		104.58(4)	
$[Cu(Me_3PS)_3(ClO_4)]$	2.007(6)	107.2(3)	*f*
	2.009(7)	104.3(3)	
	1.966 7(7)	110.3(3)	
$[Cu(Me_4P_2S_2)Cl_2]$	1.973(2)	100.71(7)	*g*
	1.995(2)	110.87(7)	
$[\{Cu(Me_4P_2S_2)Cl\}_2]$	1.995(9)	113.1(3)	*h*
	1.991(9)	109.5(3)	
$Me_3PS{\cdot}Cr(CO)_5$	1.990(3)	112.5(1)	*i*
Ph_3PSe	2.106(1)		17
$Ph_3PSe{\cdot}AlCl_3$	2.182(2)	106.95(7)	
	2.181(2)	107.15(7)	
$Ph_3PSe{\cdot}HgCl_2$	2.169(6)	98.1(1)	32
$Ph_3PSe{\cdot}AuCl$	2.187(5)	100.1(1)	33
$[Pd(CN)\{Ph_2PCH_2P(Se)Ph_2\}(SeCN)]$	2.450(2)	98.8(1)	*j*

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X-Ray Crystal Structures of $Ph_3PS{\cdot}AlCl_3$ *and* $Ph_3PSe{\cdot}AlCl_3$.—Both crystal structures consist of discrete molecular units with no unusual intermolecular contacts. While the free bases (Ph_3PS[16] and Ph_3PSe[17]) are isostructural ($P2_1/c$), the adducts assume different crystal systems (monoclinic and triclinic). Nevertheless, the structural features of the molecular units are very similar. Both molecules have a bent geometry at the chalcogen centre [P–S–Al 109.62(8); P–Se–Al(mean) 107.0(1)°]. The observed angles are typical of neutral two-co-ordinate sulphur (*e.g.* S_8, 107.8°)[18] and selenium (*e.g.* Se_8, 105.7°),[18] however, they are substantially smaller than those observed for the related oxide complexes [*e.g.* $Ph_3PO{\cdot}BF_3$, P–O–B 134.5(2);[19] $Me_3PO{\cdot}SbCl_5$, P–O–Sb 144.9(23);[20] $Ph_3PO{\cdot}AlCl_3$, P–O–Al 180;[6] $Ph_3PO{\cdot}AlBr_3$, P–O–Al 180°;[6] see also Table 7 of ref. 6]. The P–S bond length in $Ph_3PS{\cdot}AlCl_3$ [2.028(2) Å] is intermediate between that of a P–S single bond [*e.g.* $(PhS)_3P$, 2.112(1);[21] P_4S_3, P–S (mean) 2.09(1);[22] P_4S_{10}, mean 2.097(8) Å,[23] for other examples see ref. 24], and a P–S multiple bond [*e.g.* Ph_3PS, 1.950(3) Å].[16] The Al–S bond length [2.297(2) Å] is in the region of those determined for some aluminium sulphides [*e.g.* α-$ZnAl_2S_4$, Al–S 2.36(3);[25] $Ce_6Al_{10/3}S_{14}$, Al–S(tetrahedral) 2.09, 2.29, Al–S(octahedral) 2.42, 2.65; α-Al_2S_3, Al–S 2.26 Å].[26] The P–Se bonds of the two molecules in the asymmetric unit of $Ph_3PSe{\cdot}AlCl_3$ are

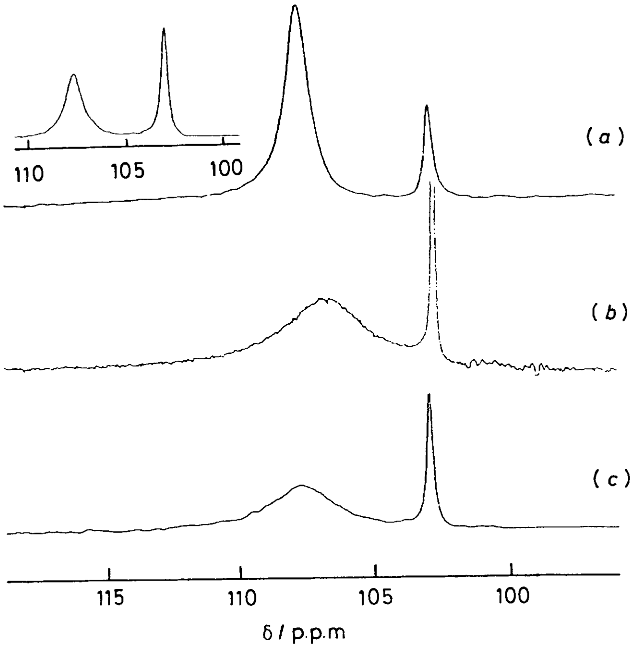
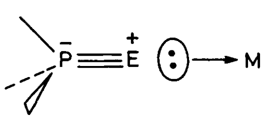


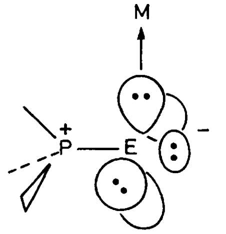
Figure 3. Aluminium-27 n.m.r. spectra of (*a*) $(Me_2N)_3PS{\cdot}AlCl_3$ (0.1 mol dm^{-3}), inset 0.02 mol dm^{-3}, (*b*) $Ph_3PSe{\cdot}AlCl_3$ (0.07 mol dm^{-3}), and (*c*) $Ph_3PS{\cdot}AlCl_3$ (0.06 mol dm^{-3})

crystallographically equivalent [2.182(2) and 2.181(2) Å] and are also intermediate between a typical P–Se single bond [*e.g.* P_4Se_3, 2.24(1);[27] $\{(Et_2N)_2PSe\}_2^{2+}$, 2.252(9) Å (average)[14]] and a P–Se multiple bond [*e.g.* Ph_3PSe, 2.106(1) Å].[17] The Al–Se bond lengths [2.452(2), 2.421(2) Å] are slightly longer than those of Al_2Se_3 (average, 2.37 Å).[28] The local environments of the phosphorus and aluminium centres are distorted tetrahedral. While the Al–Cl bond lengths are crystallographically indistinguishable in both structures, the steric constraints of the bent conformation are manifest in the slight but significant differences observed in the Cl–Al–E angles. The two molecules of $Ph_3PSe{\cdot}AlCl_3$ have significantly different $AlCl_3$ geometries, one with a single *endo* chlorine atom and the other with two *endo* chlorine atoms. In both cases, and in $Ph_3PS{\cdot}AlCl_3$, which has a single *endo* chlorine, the *endo* (inside) Cl–Al–E angles are larger than the *exo* Cl–Al–E angles. It seems that the aluminium is attempting to make contact with the phosphorus centre [$Ph_3PS{\cdot}AlCl_3$, P–Al 3.538(2); $Ph_3PSe{\cdot}AlCl_3$, P–Al 3.727(3), 3.706(3) Å], and is restricted by the steric presence of the phenyl groups. This is demonstrated by the shortest C–Cl distances [$Ph_3PS{\cdot}AlCl_3$ C(18)–C(13) 3.598(5), C(17)–C(13) 3.650(6); $Ph_3PSe{\cdot}AlCl_3$ C(8)–C(11) 3.762(8), C(26)–C(16) 3.520(8) Å], which are close to the sum of the van der Waals radii (3.55 Å).

The Phosphoryl Bond and Adduct Bonding.—The co-ordinative properties of the phosphine chalcogenides are well characterised and are generally considered to be independent of the chalcogen. However, on closer scrutiny, formation of the dative contact has an impact on the P–E bond, the nature of which is governed by both the chalcogen and the acid. While the phosphine oxides have the potential for multi-directional co-ordination (a wide range of angles is observed at the oxygen centres for complexes of phosphine oxides, see Table 7 in ref. 6), the sulphides and selenides are restricted to sharp angles of less than 116°. The examples presented above adopt typical geometries, as illustrated in Table 6 which lists a number of related compounds together with P–E bond lengths and P–E–M bond angles (M = Lewis acid). The observed bond angles are consistent with a valence shell electron pair repulsion (VSEPR) model for compounds of this type containing a two-co-ordinate chalcogen centre. However, the P–E bonds in the complexes are all significantly shorter than representative single bonds implying some retention of π bonding in the complex. Moreover, many of the observed angles are significantly smaller than 109°. On this basis, we propose a classification of the phosphine sulphides and phosphine selenides as 'side on' bonded donors or 'π donors' (organometallic terminology), employing P–E π-bonding electrons for donation, rather than σ non-bonding electrons (lone pairs). Nevertheless, as in the organometallic[29] and non-metal[30] analogues, a degree of π bonding is maintained in the base. By comparison, the phosphine oxides are able to form both 'π complexes' (side on) and 'σ complexes' (end on) depending upon the nature of the acid (see Table 7 in ref. 6). This simple view has some value in terms of developing the qualitative experimental model for the phosphoryl bond. One may conclude that the potential for σ complexation of the oxides is a consequence of effective π bonding between the phosphorus and oxygen centres, as denoted by representation (**1**),[2,*] rendering the σ-type non-bonding electrons highest in energy and therefore more available for donation. Phosphorus–chalcogen π bonding has been shown to be less pronounced in the thiophosphoryl system[2b] (this could be extrapolated to the selenophosphoryl system) and the electronic structure is more accurately denoted by representation (**2**).[2] On this basis, the electrons in π-type orbitals on sulphur or selenium may be considered more available for donation.



(**1**)



(**2**)

These fundamental differences in the dative bonding modes of the phosphine oxides and heavier phosphine chalcogenides may account for the, as yet, unexplained disparity in the ^{31}P and ^{13}C n.m.r. data for the free bases and their complexes.[4]

Complexation of Ph_3PO effects a significant change in the ^{31}P n.m.r. chemical shift, while no change is observed for the heavier triphenylphosphine chalcogenides upon complexation. The structural changes associated with complexation are in good agreement with these models. The P–O bond experiences a 3% increase in length upon adduct formation, which is essentially independent of the acid. A more dramatic 6% increase is observed for the sulphides and selenides, implying that co-ordination of the heavier chalcogenides involves a larger component of bonding electrons than for the oxides. Interestingly, structurally characterised examples of phosphine oxide complexes exhibit bond angles at oxygen of 140—180° with only two exceptions (134 and 123°).[6] In complete contrast, angles at the chalcogen in complexes of phosphine sulphides and selenides are more restricted (91—117°) and are substantially smaller (Table 6). While many of the observed conformations are strongly influenced by steric factors, the extreme non-VSEPR examples (180° for the oxides, 91° for

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[*] The common double-bonded model ($R_3P{=}E$) has been clarified by Gordon and others to be invalid.[2] The three-fold symmetry of the system requires that two equivalent π interactions take place between the phosphorus centre and the chalcogen. The system may be drawn as a combination of two resonance structures (**1**) and (**2**).

the sulphides, and 98° for the selenides) suggest important electronic control of the molecular geometry. The linear oxide adducts have no steric component and may be interpreted as 'σ complexes.' However, the short bond lengths indicate the influence of auxiliary bonding in the form of a π interaction between oxygen and aluminium, which may be partially responsible for the observed coaxial conformation.[6]

The steric constraints, which may restrict the co-ordinative requirements of the phosphine oxides (see Table 7, ref. 6), are absent in the sulphides and selenides. The very sharp angles observed for many of these complexes are consistent with 'π complexation,' assuming the interaction with phosphorus is limited by the steric presence of the groups attached to phosphorus, and that the sulphur or selenium centres carry the bulk of the electron density in the donor orbital. Consequently, the phosphine chalcogenides act as 'π donors' having extremely distorted (or polarised) π clouds.[30,31] The asymmetric distortions of the $AlCl_3$ unit from tetrahedral geometry observed in the structures of $Ph_3PS{\cdot}AlCl_3$ and $Ph_3PSe{\cdot}AlCl_3$ (with the chlorine atoms displaced away from the phosphine unit) allow a contact between the phosphorus and aluminium centres. Similar features are reported for the severely bent phosphine selenide complexes $Ph_3PSe{\cdot}HgCl_2$ (Hg–P 3.53 Å)[32] and $Ph_3PSe{\cdot}AuCl$ [3.497(7) Å],[33] and are rationalised in terms of repulsions between non-bonding electrons on the selenium centre. We consider the observations to be indicative of an incipient interaction between the phosphorus and metal centres, and the distortions observed at the aluminium centre to be the result of the molecules achieving the steric limit for interactions between the $AlCl_3$ and PPh_3 units. In conclusion the heavier phosphine chalcogenides adopt a different dative bonding mode to that for the phosphine oxides.

Acknowledgements

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