Chemistry of the Diaminochalcogenophosphinic Chloride–Aluminium Trichloride System: Preparation and Crystal Structures of New Chalcogenophosphonium Cations§

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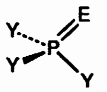
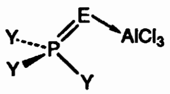
A comprehensive investigation of the reactions between diaminothiophosphinic chlorides, $(R_2N)_2P(S)Cl$ (R = Me, Et, or Pr^i), and aluminium trichloride confirms the potential for at least two modes of reactivity. Typical Lewis acid–base complexes have been observed at room temperature in solution by ^{31}P and ^{27}Al n.m.r. spectroscopy. However, in the solid state, novel dimeric heterocyclic diphosphonium systems have been isolated for the Me_2N and Et_2N derivatives (crystal data for $[\{(Et_2N)_2PS\}_2][AlCl_4]_2$: monoclinic, space group $P2_1/n$, $a = 10.598(2)$, $b = 8.976(2)$, $c = 19.370(4)$ Å, $\beta = 98.65(2)°$, $Z = 2$, $R = 0.052$). In contrast, the $Pr^i{}_2N$ derivative maintains the covalent Lewis acid–base adduct structure in the solid state [crystal data for $(Pr^i{}_2N)_2P(Cl)S\cdot AlCl_3$: monoclinic, space group $P2_1/c$, $a = 12.705(5)$, $b = 9.504(3)$, $c = 18.016(6)$ Å, $\beta = 92.85(3)°$, $Z = 4$, $R = 0.066$]. The diaminoselenophosphinic chlorides show no evidence of adduct formation in solution; however, identical heterocyclic diphosphonium salts have been isolated in the solid state for the Me_2N and Et_2N derivatives (crystal data for $[\{(Et_2N)_2PSe\}_2][AlCl_4]_2$: triclinic, space group $P\bar{1}$, $a = 10.635(7)$, $b = 12.335(8)$, $c = 15.159(9)$ Å, $\alpha = 95.94(8)$, $\beta = 93.46(7)$, $\gamma = 110.99(9)°$, $Z = 2$, $R = 0.066$). The new heterocycles represent examples of heterocyclic thiophosphonium (and selenophosphonium) cations, and are structurally related to known neutral isovalent phosphetanes. In solution, the thiophosphonium salts dissociate and reform the Lewis acid–base adducts, while the selenium analogues adopt an equilibrium involving only ionic species. The delicate energetic balance between ionic and covalent structures is further demonstrated for the sulphur systems by the promotion of the ionic structures in solutions containing an excess of $AlCl_3$. However, the solution species react with CH_2Cl_2 by means of an electrophilic attack at the sulphur centre.

The chemistry of the chalcogenophosphoryl unit (1) (E = O, S, or Se; Y = R, NR_2, OR, X, *etc.*) has been investigated extensively.[1] The most common mode of reactivity is Lewis base behaviour involving the E centre as in (2).[2] However, the reaction of $P(S)Cl_3$ with $AlCl_3$ is reported to produce both Lewis acid–base complexes and salts of the form $P(S)Cl_2{}^+$ $AlCl_4{}^-$.[3] Similarly, reactions of phosphinimine halides $[Y_2P(E)Cl$, E = NR] with Lewis acids are reported to initially form adducts, which undergo halide-ion abstraction from the phosphorus centre to give the isomeric salt upon heating.[4] Unfortunately, experimental evidence is limited for both systems, and other related systems appear complex and are incompletely characterised.[5] Nevertheless, two reactive sites are evident for phosphoryl derivatives possessing a labile ligand in one or more of the Y positions [*e.g.*, $Y_2P(E)Cl$].



(1)



(2)

In view of the predominance of the halide-ion abstraction process as a synthetic method in non-metal chemistry,[6] we have attempted to establish both the co-ordinative and the dissociative potential of the phosphinic halide system more accurately. Here we present conclusive studies on the chemistry of diaminothio- and diaminoseleno-phosphinic chlorides with aluminium trichloride. The results confirm the formation of covalent complexes for the thio derivatives, but demonstrate a small thermodynamic preference for novel dichalcogenodiphosphonium ionic alternatives.

Experimental

General Procedures.—The compounds Me_2NH, Et_2NH, $Pr^i{}_2NH$, PCl_3, S_8, and Se were obtained commercially and used without purification. Anhydrous $AlCl_3$ and $GaCl_3$ (Aldrich) were sublimed under vacuum before use. Dichloromethane was dried over P_2O_5 and CaH_2 and stored in an evacuated bulb; $CDCl_3$ was dried three times over P_2O_5. The compounds $(Pr^i{}_2N)_2PCl$,[7] $(Me_2N)_2P(S)Cl$,[8] $(Et_2N)_2P(S)Cl$,[8] $(Me_2N)_2P(Se)Cl$[9] and $(Et_2N)_2P(Se)Cl$[9] were prepared by literature methods, and characterised by the usual techniques. All aluminium containing solids were manipulated in a Vacuum/Atmospheres nitrogen-filled glove-box. Glass equipment was flame dried before use. Reactions were performed in an evacuated (10^{-3} Torr, 0.133 Pa) dual-compartment vessel, a modification of the H-tube reaction vessel described in ref. 10. Melting points were recorded on a Fisher-Johns apparatus and are uncorrected. Elemental analyses were performed by Beller Laboratories, Göttingen, Germany. I.r. spectra were recorded as Nujol mulls or neat liquids on CsI plates using a Perkin-

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

Table 1. Phosphorus-31 and ^{13}C n.m.r. data in CH_2Cl_2

Compound	$\delta(^{31}P)$/p.p.m.	$\delta(^{13}C)$/p.p.m.
$(Me_2N)_2P(S)Cl$	91.5	37.2
$(Et_2N)_2P(S)Cl$	84.6	
$(Pr^i{}_2N)_2P(S)Cl$	69.8[a]	48.1, 22.2, 21.9[a]
$(Me_2N)_2P(Cl)S{\cdot}AlCl_3$	78.6	38.3
$(Et_2N)_2P(Cl)S{\cdot}AlCl_3$	72.5	42.0, 13.0
$(Pr^i{}_2N)_2P(Cl)S{\cdot}AlCl_3$	63.2[a]	50.1, 22.6, 22.4[a]
$(Me_2N)_3PS$	82.2	
$(Me_2N)_3PS{\cdot}AlCl_3$	68.6	37.6
Ph_3PS	43.2	
$Ph_3PS{\cdot}AlCl_3$	42.8	
$(Me_2N)_2P(Cl)SCH_2Cl^+$	73.0	44.9, 38.6
$(Et_2N)_2P(Cl)SCH_2Cl^+$	69.0	45.4, 43.0, 13.3
$(Pr^i{}_2N)_2P(Cl)SCH_2Cl^+$	60.5	51.5, 45.2, 22.9, 21.5
$(Me_2N)_2P(Se)Cl$	84.8[a] (901[b])	37.7[a]
$(Et_2N)_2P(Se)Cl$	74.9 (893[b])	
$(Pr^i{}_2N)_2P(Se)Cl$	52.7[a] (881[b])	48.5, 22.6, 21.8[a]
$(Me_2N)_2P(Se)Cl{-}AlCl_3$	267, 50—80[c]	
$(Et_2N)_2P(Se)Cl{-}AlCl_3$	264.0, 79—80, −7.8 (341[b])	
$(Pr^i{}_2N)_2P(Se)Cl{-}AlCl_3$	313.2	

[a] Recorded in $CDCl_3$. [b] J_{PSe}/Hz. [c] More than 20 peaks.

Elmer 283B spectrophotometer. N.m.r. spectra were recorded on a Nicolet NT-360 spectrometer in CH_2Cl_2 (unless otherwise stated) in 10-mm pyrex tubes. The ^{31}P and ^{13}C n.m.r. data are presented in Table 1. 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} and relative to the internal solvent signal for ^{13}C spectra. Mass spectra were obtained by using a CEC model 21-104 mass spectrometer.

I.r. data. $(Et_2N)_2P(S)Cl$: 1 300s, 1 255w, 1 205s, 1 165s, 1 105s, 1 065s, 1 025s, 945s, 790s, 735s, 695s, 610s, 500s, 440w, 390w, 340m, and 245m cm^{-1}.

$(Et_2N)_2P(Se)Cl$: 1 300s, 1 260w, 1 205s, 1 165s, 1 025s, 950s, 790s, 685s, 555s, 505m, 470w, 430w, and 330m cm^{-1}.

Preparation of Bis(di-isopropylamino)chalcogenophosphinic Chloride $(Pr^i{}_2N)_2P(E)Cl$ (E = S* *or* Se).—A stirred mixture of $(Pr^i{}_2N)_2PCl$ (E = S, 3.12 g, 11.7 mmol; E = Se, 4.26 g, 16.0 mmol), elemental chalcogen (S_8, 0.38 g, 11.9 mmol; Se, 1.63 g, 16.0 mmol), and $AlCl_3$ (E = S, 0.08 g, 0.56 mmol; E = Se, 0.13 g, 0.94 mmol) in CH_2Cl_2 (E = S, 25.7 g; E = Se, 25 g) was heated (E = S, 60 °C for 24 h; E = Se, 95—100 °C for 70 h).

E = S. The solvent was removed to yield an orange-yellow solid which was vacuum sublimed twice at 80 °C and recrystallised from hot hexane to give large white elongated crystals of $(Pr^i{}_2N)_2P(S)Cl$. Yield: 1.69 g, 5.67 mmol, 50%; m.p. 105 °C; mass spectrum [*m*/*z* (relative intensity)]: 298 (11), 166 (28), and 100 (100); (Found: C, 48.05; H, 9.25; N, 9.40; P, 10.30; S, 10.85. Calc. for $C_{12}H_{28}ClN_2PS$: C, 48.25; H, 9.45; N, 9.35; P, 10.35; S, 10.75%). I.r.: 1 195s, 1 170s, 1 155s, 1 120s, 990vs, 970vs, 880w, 850w, 840w, 705vs, 650w, 595m, 550m, 535m, 495m, 430m, and 385w cm^{-1}.

E = Se. The solvent was removed and the resulting solid was extracted with hexane (14 g) to leave a green precipitate and an orange solution. The orange slurry produced upon removal of the hexane was vacuum sublimed three times at 95 °C and recrystallised from hot hexane to give large white elongated crystals of $(Pr^i{}_2N)_2P(Se)Cl$. Yield: 0.794 g, 2.3 mmol, 15%; m.p. 111—112 °C; mass spectrum [*m*/*z* (relative intensity)]: 346 (8), 266 (18), 231 (18), and 166 (100); (Found: C, 42.05; H, 8.45; N, 8.00. Calc. for $C_{12}H_{28}ClN_2PSe$: C, 41.70; H, 8.15; N, 8.10%). I.r.: 1 195s, 1 170s, 1 150s, 1 115s, 990vs, 970vs, 875w, 850w, 840w, 640s, 565s, 550m, 535m, 495m, 465w, 415w, and 385w cm^{-1}.

Preparation of 2,2,4,4-*Tetrakis(dialkylamino)*-2λ^5,4λ^5-*cyclodi(phosphoniathiane) Bis(tetrachloroaluminate)* (*Alkyl* = Me *or* Et).—A solution of $(R_2N)_2P(S)Cl$ (R = Me, 0.493 g, 2.64 mmol; R = Et, 5.03 g, 20.7 mmol) in CH_2Cl_2 (R = Me, 20 cm^3; R = Et, 69 g) was added to $AlCl_3$ (R = Me, 0.353 g, 2.64 mmol; R = Et, 2.77 g, 20.7 mmol) and the mixture was stirred at room temperature. A vigorous reaction occurred with solvation of $AlCl_3$. After several hours the solvent was removed slowly from the clear pale yellow solution to yield white crystals. The supernatant liquid was decanted and the crystals were washed in cooled solvent by local cooling back distillation of CH_2Cl_2.

R = Me. The crystals were characterised as $[\{(Me_2N)_2PS\}_2][AlCl_4]_2$. Yield: 0.65 g, 1.02 mmol, 77%; m.p. 128 °C; mass spectrum [*m*/*z* (relative intensity)]: 284 (13), 186 (18), 151 (19), 142 (31), and 44 (100) (Found: C, 15.10; H, 3.65; N, 8.65; P, 9.50; S, 9.90. Calc. for $C_8H_{24}Al_2Cl_8N_4P_2S_2$: C, 15.00; H, 3.80; N, 8.75; P, 9.70; S, 10.00%). I.r.: 1 300m, 1 160m, 1 055m, 1 010s, 985s, 760w, 705m, 665w, 635m, 615w, 485vs br, 370w, and 305w cm^{-1}.

R = Et. The crystals were characterised as $[\{(Et_2N)_2PS\}_2][AlCl_4]_2$. Yield: 6.688 g, 8.89 mmol, 86%; m.p. 100 °C; mass spectrum [*m*/*z* (relative intensity)]: 242 (21), 207 (25), and 72 (100); (Found: C, 25.60; H, 5.35; N, 7.30. Calc. for $C_{16}H_{40}Al_2Cl_8N_4P_2S_2$: C, 25.55; H, 5.35; N, 7.45%). I.r.: 1 300m, 1 205s, 1 150s, 1 100m, 1 065m, 1 025s, 960m, 930m, 840w, 790s, 745m, 705w, 675m, 630m, 490vs br, and 350m cm^{-1}.

Preparation of Bis(di-isopropylamino)thiophosphinic Chloride–Aluminium Trichloride Adduct.—A solution of $(Pr^i{}_2N)_2P(S)Cl$ (1.075 g, 3.6 mmol) in CH_2Cl_2 (13.7 g) was added to $AlCl_3$ (0.485 g, 3.63 mmol) and shaken until solvation of $AlCl_3$ was complete. Slow removal of solvent from the clear reaction mixture gave small white crystals. The supernatant liquid was decanted and the crystals were washed twice with small aliquots of cool CH_2Cl_2, and characterised as the $(Pr^i{}_2N)_2P(Cl)S{\cdot}AlCl_3$ adduct. Yield: 1.28 g, 2.96 mmol, 82%; m.p. 152 °C; mass spectrum [*m*/*z* (relative intensity)]: 298 (6), 163 (28), 120 (24), and 100 (100); (Found: C, 33.20; H, 6.55; N, 6.45; P, 7.35; S, 7.50. Calc. for $C_{12}H_{28}AlCl_4N_2PS$: C, 33.35; H, 6.55; N, 6.50; P, 7.15; S, 7.40%). I.r.: 1 195s, 1 165s, 1 140s, 1 110s, 1 005vs, 995vs, 965vs, 875w, 845m, 640s, 595vs, 550s, 515vs, 500vs, 440s, and 415s cm^{-1}.

The $(Pr^i{}_2N)_2P(Cl)S{\cdot}GaCl_3$ adduct was prepared in a similar manner to the aluminium derivative. Yield: 53%; m.p. 184 °C. I.r.: 1 195s, 1 165s, 1 140s, 1 110s, 1 005vs, 995vs, 965vs, 875w, 845m, 640s, 595vs, 550s, 510w, 470w, 390s, 375s, and 350s cm^{-1}.

Preparation of 2,2,4,4-*Tetrakis(dialkylamino)*-2λ^5,4λ^5-*cyclodi(phosphoniaselenone) Bis(tetrachloroaluminate)* (*Alkyl* = Me *or* Et).—A solution of $(R_2N)_2P(Se)Cl$ (R = Me, 1.01 g, 4.33 mmol; R = Et, 2.24 g, 7.74 mmol) in CH_2Cl_2 (R = Me, 15.4 g; R = Et, 26.3 g) was added to $AlCl_3$ (R = Me, 0.58 g, 4.36 mmol; R = Et, 1.03 g, 7.74 mmol) and the mixture was stirred at room temperature. Yellow solutions were formed rapidly and the $AlCl_3$ was consumed.

R = Me. Precipitation of a pale yellow solid occurred within seconds. The orange solution was decanted and the solid was washed by back distillation of solvent, and characterised as $[\{(Me_2N)_2PSe\}_2][AlCl_4]_2$. Yield: 0.796 g, 1.08 mmol, 50%; m.p. 128 °C; mass spectrum [*m*/*z* (relative intensity)]: 234 (41), 199 (13), 154 (20), 119 (26), and 110 (100). I.r.: 1 290m, 1 150m, 1 050m, 995s, 970s, 685m, 545w, and 480vs cm^{-1}.

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* Previously observed as a reaction by-product, but not characterised.[11]

R = Et. The solution went through a number of colour changes (yellow, orange, red, orange, and yellow). After 4 h, the solvent was removed slowly to give bright yellow crystals of $[\{(Et_2N)_2PSe\}_2][AlCl_4]_2$. Yield: 3.118 g, 3.68 mmol, 95%; m.p. 119 °C; mass spectrum [m/z (relative intensity)]: 290 (16), 255 (11), 210 (3), and 138 (100); (Found: C, 22.65; H, 4.95; N, 6.60; P, 7.30; Se, 18.65. Calc. for $C_{16}H_{40}Al_2Cl_8N_4P_2Se_2$: C, 22.70; H, 4.75; N, 6.60; P, 7.30; Se, 18.65%). I.r.: 1 290w, 1 205s, 1 145m, 1 100m, 1 050m, 1 015s, 980w, 955m, 925w, 795s, 660w, 540w, and 485vs cm^{-1}.

N.m.r. Studies of Reactions Between $(R_2N)_2P(E)Cl$ (R = Me, Et, *or* Pr^i; E = S *or* Se) *and* $AlCl_3$.—Equimolar reaction mixtures of the phosphinic chlorides and $AlCl_3$ in CH_2Cl_2 were examined by ^{13}C, ^{31}P, and ^{27}Al n.m.r. spectroscopy. Characteristic spectra for Lewis acid–base complexes of the form $(R_2N)_2P(Cl)S{\cdot}AlCl_3$ were observed for all of the sulphur derivatives,[2] as quantitative solution products. For the Me/Se and Et/Se derivatives, a number of signals were observed in the ^{31}P spectra and a single sharp line at 102 p.p.m. in the ^{27}Al spectra corresponding to $AlCl_4^-$.[12] The ^{31}P and ^{27}Al spectra of the Pr^i/Se system show $(Pr^i_2N)_2P^+AlCl_4^-$ to be the only species in solution.[6b] A red precipitate was isolated from the reaction mixture which gave no bands in the i.r. spectrum, indicative of it being elemental selenium.

Variable-temperature ^{31}P *N.m.r. Studies on the Dissolution of* $[\{(Et_2N)_2PS\}_2][AlCl_4]_2$.—A sample of $[\{(Et_2N)_2PS\}_2][AlCl_4]_2$ (0.052 g) was placed in a 10 mm n.m.r. tube and CH_2Cl_2 (3 cm^3) was introduced at −198 °C. The sample was warmed to −78 °C immediately prior to placement in the n.m.r. probe, which had been cooled previously to −70 °C. Each spectrum was obtained after a 5 min temperature equilibration period. The spectra were observed during data acquisition and therefore spectra for a particular temperature represent an average over the data acquisition period. After 20 min at −70 °C, 30 min at −40 °C, and 10 min at −20 °C, no signals were observed. After 15 min at 0 °C, two single peaks were observed at 75 (20) and 21 p.p.m. (80%). After 5 min at 20 °C, the signal at 75 p.p.m. was not observed and the peak at 21 p.p.m. (70%) dominated the spectrum, with a new signal at 22 p.p.m. (30%) observed as a shoulder. The signal at 22 p.p.m. increased over the next 5 min and became the dominant peak. After 30 min two small peaks of approximately equal intensity were also observed at 75 and 73 p.p.m. After another 2 h at room temperature (22 °C) the spectrum consisted of a small peak at 75 p.p.m. and two equal intensity peaks at 73 and 22 p.p.m. Complete dissolution of the crystals occurred on standing at room temperature for 3 d, and the spectrum contained only the signal at 73 p.p.m. which corresponds to $(Et_2N)_2P(Cl)S{\cdot}AlCl_3$.

N.m.r. Studies of the Reactions Between $(R_2N)_2P(Cl)S{\cdot}AlCl_3$ *and Excess* $AlCl_3$.—Three solutions: $[\{(Me_2N)_2PS\}_2][AlCl_4]_2$ (0.06 g, 0.08 mmol) and $AlCl_3$ (0.06 g, 0.4 mmol) in CH_2Cl_2 (3.85 g), $[\{(Et_2N)_2PS\}_2][AlCl_4]_2$ (0.04 g, 0.05 mmol) and $AlCl_3$ (0.03 g, 0.2 mmol) in CH_2Cl_2 (3.85 g), and $(Pr^i_2N)_2P(S)Cl$ (0.03 g, 0.1 mmol) and $AlCl_3$ (0.03 g, 0.2 mmol) in CH_2Cl_2 (1.70 g), were prepared and studied by ^{31}P n.m.r. spectroscopy. After 5 d the spectra showed signals at: R = Me, 78 (30), 73 (20), and 27 p.p.m. (50%); R = Et, 73 (10), 69 (20), and 21 p.p.m. (70%); R = Pr^i, 60 (60) and 18 p.p.m. (40%).

N.m.r. Studies on the Reaction of $(R_2N)_2P(Cl)S{\cdot}AlCl_3$ (R = Me, Et, *or* Pr^i) *with* CH_2Cl_2.—N.m.r. samples of $[\{(Me_2N)_2PS\}_2][AlCl_4]_2$ (0.06 g), $[\{(Et_2N)_2PS\}_2][AlCl_4]_2$ (0.03 g) and $(Pr^i_2N)_2P(Cl)S{\cdot}AlCl_3$ (0.11 g) in CH_2Cl_2 (3.55, 2.47, and 3 g, respectively) were warmed to 80 °C for 24 h. ^{31}P N.m.r. spectra showed the quantitative formation of new species with chemical shifts of 73, 70, and 60 p.p.m., respectively. The ^{27}Al n.m.r. spectra of all three solutions consist of only a single sharp peak at 102 p.p.m. (corresponding to $AlCl_4^-$).[12] In a preparative experiment $(Pr^i_2N)_2P(Cl)S{\cdot}AlCl_3$ (0.66 g, 1.5 mmol) was dissolved in CH_2Cl_2 (17.8 g) and the solution was heated to 80 °C for 18 h. After removal of the solvent the sample weight had increased by 0.13 g, corresponding to an uptake of CH_2Cl_2 (1.5 mmol).

X-Ray Data Collection, Solution, and Refinement.—Crystals of $[\{(Et_2N)_2PS\}_2][AlCl_4]_2$ (colourless), $[\{(Et_2N)_2PSe\}_2][AlCl_4]_2$ (yellow), and $(Pr^i_2N)_2P(Cl)S{\cdot}AlCl_3$ (colourless) suitable for *X*-ray crystallography were obtained from saturated solutions of CH_2Cl_2 by slow removal of the solvent under vacuum. Crystals were selected in the dry-box and mounted in thin-walled Pyrex capillaries under nitrogen. An Enraf-Nonius CAD-4 diffractometer using Mo-K_α radiation (λ = 0.710 73 Å) was used to determine the cell dimensions and to collect the data. The crystal data and data-collection parameters are presented in Table 2. Data were collected using an ω—2θ scan (width $0.80 + 0.35 \tan\theta$) over a 2θ range of $2 \leqslant 2\theta \leqslant 50°$. Scattering factors for neutral atoms were corrected for anomalous dispersion.[13] The structures were solved by direct methods (MULTAN)[14] and refined by a full-matrix least-squares procedure[15] using anisotropic thermal parameters for all non-hydrogen atoms. The geometrically constrained 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 $Å^2$. The methyl hydrogen atoms were included as rigid groups with rotational freedom at the bonded carbon atom (C–H = 0.95 Å, B = 5.5 $Å^2$).

$[\{(Et_2N)_2PS\}_2][AlCl_4]_2$. The space group was determined to be the centric $P2_1/n$ from the systematic absences. Least-squares refinement with isotropic thermal parameters led to R = 0.121. Refinement of the non-hydrogen atoms with anisotropic thermal parameters led to the final values of R = 0.052 and R' = 0.056.

$[\{(Et_2N)_2PSe\}_2][AlCl_4]_2$. The space group was determined to be either the centric $P\bar{1}$ or acentric $P1$. Statistical tests indicated that the space group was centric and the subsequent solution and successful refinement of the structure in the space group $P\bar{1}$ confirmed this. Least-squares refinement with isotropic thermal parameters led to R = 0.131. Refinement of the non-hydrogen atoms with anisotropic thermal parameters led to the final values of R = 0.066 and R' = 0.069.

$(Pr^i_2N)_2P(Cl)S{\cdot}AlCl_3$. The space group was determined to be $P2_1/c$ from systematic absences. Refinement of the non-hydrogen atoms with anisotropic thermal parameters led to the final values of R = 0.066 and R' = 0.078.

The final fractional atomic co-ordinates for $[\{(Et_2N)_2PS\}_2][AlCl_4]_2$, $[\{(Et_2N)_2PSe\}_2][AlCl_4]_2$, and $(Pr^i_2N)_2P(Cl)S{\cdot}AlCl_3$ are given in Tables 3—5, respectively and selected bond distances and angles in Tables 6—8, respectively. Views of the molecules are given in Figures 1—3, respectively.[16]

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

Results and Discussion

Reactions Between Bis(dialkylamino)chalcogenophosphinic Chlorides and $AlCl_3$.—Addition of a series (R = Me, Et, or Pr^i) of bis(dialkylamino)thiophosphinic chlorides, $(R_2N)_2P(S)Cl$, in CH_2Cl_2 to $AlCl_3$ under anhydrous conditions at room temperature results in the formation of Lewis acid–base complexes in solution. The ^{27}Al n.m.r. spectral patterns observed for the reaction mixtures contain a sharp signal at 102 p.p.m. ($AlCl_4^-$),[12] with a more substantial (> 80%) broad peak slightly

Table 2. Crystal data collection and refinement parameters for $[\{(Et_2N)_2PS\}_2][AlCl_4]_2$, $[\{(Et_2N)_2PSe\}_2][AlCl_4]_2$, and $(Pr^i_2N)_2P(Cl)S{\cdot}AlCl_3$

Formula	$C_8H_{20}Al_2Cl_8N_4P_2S_2$	$C_8H_{20}Al_2Cl_8N_4P_2Se_2$	$C_{12}H_{28}AlCl_4N_2PS$
M	752.19	846.0	432.20
Crystal class	Monoclinic	Triclinic	Monoclinic
Space group	$P2_1/n$	$P\bar{1}$	$P2_1/c$
Cell constants	25 refl. θ > 21°	23 refl. θ > 20°	21 refl. θ > 15°
a/Å	10.598(2)	10.635(7)	12.705(5)
b/Å	8.976(2)	12.335(8)	9.504(3)
c/Å	19.370(4)	15.159(9)	18.016(6)
α/°	—	95.94(8)	—
β/°	98.65(2)	93.46(7)	92.85(3)
γ/°	—	110.99(9)	—
U/Å^3	1 822	1 836.5	2 173
Z	2	2	4
$F(000)$	640	712	904
D/g cm^{-3}	1.37	1.53	1.32
Crystal size/mm	0.05 × 0.40 × 0.33	0.20 × 0.40 × 0.40	0.20 × 0.20 × 0.23
$\mu_{calc.}$/cm^{-1}	8.1	26.3	7.43
Standard reflections	6, 0, 0; 0, 4, 0; 0, 0, 16	5, 0, 0; 0, 8, 0; 0, 0, 11	4, 0, 0; 0, 2, 0; 0, 0, 6
Decay of standards	±1%	±2%	±2%
Range of h, k, l	+12, +10, ±23	+12, ±14, ±18	+15, +11, ±21
Reflections measured	3 598	5 621	4 227
Observed reflections $[F_o > 5\sigma(F_o)]$	1 544	3 276	1 068
Parameters	166	331	214
Weights $w = [\sigma^2(F_o) + xF_o^2]^{-1}$			
$x =$	0.000 4	0.000 09	0.001 0
Goodness-of-fit[a]	0.91	2.31	0.81
R[b]	0.052	0.066	0.066
R'[c]	0.056	0.069	0.078
Largest feature in final difference map/e Å^{-3}	0.4	0.8	0.4

[a] Goodness-of-fit = $\{\Sigma w(\|F_o| - |F_c\|)^2/(\text{No. of reflections} - \text{No. of Parameters})\}^{\frac{1}{2}}$. [b] $R = \Sigma\|F_o| - |F_c\|/\Sigma|F_o|$.
[c] $R' = \{\Sigma w(\|F_o| - |F_c\|)^2/\Sigma(w|F_o|)^2\}^{\frac{1}{2}}$.

Table 3. Final fractional atomic co-ordinates for $[\{(Et_2N)_2PS\}_2]$-$[AlCl_4]_2$

Atom	X/a	Y/b	Z/c
S	0.894 5(2)	0.111 0(2)	0.967 54(9)
P	0.908 2(2)	−0.089 2(2)	1.025 18(9)
N(1)	0.868 6(5)	−0.070 8(6)	1.101 2(2)
N(2)	0.824 9(5)	−0.214 7(6)	0.980 1(3)
C(1)	0.952 9(7)	−0.102 6(9)	1.168 9(3)
C(2)	0.915(1)	−0.236(1)	1.204 1(5)
C(3)	0.738 0(6)	−0.016 1(9)	1.105 5(4)
C(4)	0.739(1)	0.139(1)	1.136 2(5)
C(5)	0.835 8(8)	−0.233 5(9)	0.905 0(4)
C(6)	0.718(1)	−0.190(1)	0.858 2(5)
C(7)	0.754 1(7)	−0.331 0(8)	1.010 3(4)
C(8)	0.832(1)	−0.469(1)	1.027 3(5)
Al	0.566 5(2)	0.293 7(3)	0.851 0(1)
Cl(1)	0.751 7(2)	0.373 6(3)	0.839 2(1)
Cl(2)	0.439 8(3)	0.473 6(3)	0.855 2(1)
Cl(3)	0.577 5(2)	0.172 4(3)	0.946 0(1)
Cl(4)	0.497 6(3)	0.154 6(3)	0.765 6(1)

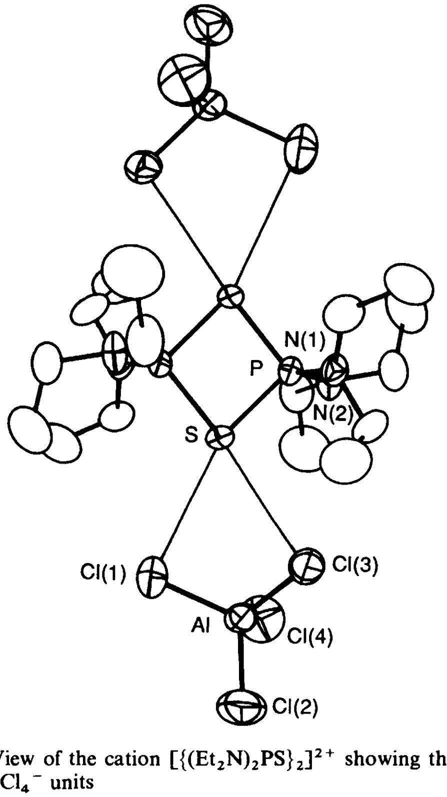


Figure 1. View of the cation $[\{(Et_2N)_2PS\}_2]^{2+}$ showing the contacts with the $AlCl_4^-$ units

downfield (106 p.p.m.), and are characteristic of phosphine chalcogenide adducts of $AlCl_3$, (**2**) [*e.g.* $(Me_2N)_3PS{\cdot}AlCl_3$ and $Ph_3PS{\cdot}AlCl_3$].[2b] The ^{31}P n.m.r. spectra for all of these reaction solutions show single peaks with a chemical shift slightly shielded from the corresponding free bases (thiophosphinic chloride), again typical for phosphine chalcogenide–aluminium trichloride complexes[2b] (see Table 1).

In contrast, reactions between $(R_2N)_2P(Se)Cl$ (R = Me, Et, or Pr^i) and $AlCl_3$ produce exclusively ionic species in solution, as indicated by ^{27}Al n.m.r. (102 p.p.m., $AlCl_4^-$)[12] The ^{31}P n.m.r. spectra show $(Me_2N)_2P^+$ (268 p.p.m.)[6b] or $(Et_2N)_2P^+$ (264 p.p.m.)[6b] as one of a number of species in solution for the Me/Se or Et/Se system, respectively. Complex equilibria are evident in the Et/Se system, involving the dimeric dication (see later) $[\{(Et_2N)_2PSe\}_2]^{2+}$ (^{31}P n.m.r. −7.8 p.p.m., J_{PSe} = 341 Hz, also observed as a triplet in the ^{77}Se n.m.r. spectrum, J_{PSe} = 340 Hz), and other unidentified species. The ion $(Pr^i_2N)_2P^+$ (313

Table 4. Final fractional atomic co-ordinates for $[\{(Et_2N)_2PSe\}_2][AlCl_4]_2$

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Se(1)	0.403 3(1)	0.475 3(1)	0.770 04(9)
Se(2)	0.099 4(1)	0.505 3(1)	0.755 53(9)
P(1)	0.317 4(3)	0.613 6(3)	0.745 0(2)
P(2)	0.186 2(3)	0.366 9(3)	0.779 7(2)
N(1)	0.332 9(9)	0.661 9(9)	0.649 7(6)
N(2)	0.379(1)	0.720 9(8)	0.821 0(6)
N(3)	0.134(1)	0.257 2(8)	0.702 9(6)
N(4)	0.149 7(9)	0.325 8(8)	0.876 5(6)
C(1)	0.260(2)	0.579(1)	0.567 3(9)
C(2)	0.341(2)	0.516(2)	0.524(1)
C(3)	0.436(1)	0.766(1)	0.631 9(9)
C(4)	0.394(2)	0.852(1)	0.590(1)
C(5)	0.486(2)	0.735(1)	0.895 3(9)
C(6)	0.596(2)	0.846(1)	0.908(1)
C(7)	0.317(1)	0.808(1)	0.830 3(9)
C(8)	0.258(2)	0.826(2)	0.913(1)
C(9)	0.221(1)	0.220(1)	0.641 4(8)
C(10)	0.202(2)	0.096(1)	0.644(1)
C(11)	−0.015(1)	0.192(1)	0.685 8(8)
C(12)	−0.080(2)	0.198(2)	0.594(1)
C(13)	0.178(1)	0.417(1)	0.954 7(8)
C(14)	0.294(2)	0.421(2)	1.016 1(9)
C(15)	0.119(1)	0.202(1)	0.893 9(8)
C(16)	−0.011(2)	0.155(2)	0.938(1)
Al(1)	0.871 6(4)	0.772 0(4)	0.694 5(3)
Cl(1)	0.809 2(4)	0.865 6(4)	0.601 2(2)
Cl(2)	0.998 0(5)	0.693 4(5)	0.636 3(3)
Cl(3)	0.696 7(5)	0.643 3(4)	0.728 2(3)
Cl(4)	0.978 7(6)	0.890 7(4)	0.808 4(3)
Al(2)	−0.368 4(4)	0.244 1(4)	0.780 9(3)
Cl(5)	−0.533 9(4)	0.247 6(4)	0.851 3(2)
Cl(6)	−0.360 6(5)	0.077 2(3)	0.764 4(3)
Cl(7)	−0.185 2(4)	0.361 4(4)	0.857 6(3)
Cl(8)	−0.389 3(6)	0.301 3(5)	0.657 1(3)

Table 5. Final fractional atomic co-ordinates for $(Pr^i{}_2N)_2P(Cl)S\cdot AlCl_3$

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
P	0.251 4(3)	0.104 0(5)	0.074 2(2)
S	0.162 2(3)	0.008 3(5)	−0.006 6(2)
Al	0.259 5(4)	−0.136 3(5)	−0.078 4(3)
Cl(1)	0.403 0(3)	0.070 8(5)	0.058 4(2)
Cl(2)	0.341 6(4)	−0.014 0(6)	−0.154 3(3)
Cl(3)	0.361 3(4)	−0.276 1(6)	−0.019 9(3)
Cl(4)	0.133 1(4)	−0.247 9(6)	−0.132 8(3)
N(1)	0.225 3(9)	0.273(1)	0.071 8(7)
N(2)	0.230 0(8)	0.043(1)	0.157 3(6)
C(1)	0.256(1)	0.360(2)	0.140 8(8)
C(2)	0.363(1)	0.432(2)	0.131(1)
C(3)	0.167(1)	0.456(2)	0.158(1)
C(4)	0.209(1)	0.356(2)	0.001 7(9)
C(5)	0.284(2)	0.336(2)	−0.058 3(9)
C(6)	0.094(2)	0.349(2)	−0.028(1)
C(7)	0.116(1)	0.044(2)	0.174 9(9)
C(8)	0.101(1)	0.111(2)	0.252 0(9)
C(9)	0.071(2)	−0.103(2)	0.169(1)
C(10)	0.302(1)	−0.034(2)	0.209 4(8)
C(11)	0.385(1)	0.061(3)	0.246(1)
C(12)	0.344(2)	−0.170(2)	0.179(1)

p.p.m.)[6b] is the only phosphorus containing species in the reaction of $(Pr^i{}_2N)_2P(Se)Cl$ with $AlCl_3$, and precipitation of elemental selenium renders the process irreversible.

Removal of solvent from the reaction solutions provides good yields (>75%) of crystalline solids (the low solubility of the precipitate obtained from the Me/Se system has prevented yield optimisation) with the empirical formulae $R_4N_2PEAlCl_4$. In contrast to the solution chemistry, *X*-ray crystallographic analysis of the Et/S and Et/Se derivatives of $R_4N_2PEAlCl_4$ show them to be salts of heterocyclic dimeric cations (**3**) (Y = NR_2) (see later).

Table 6. Bond distances (Å) and angles (°) for $[\{(Et_2N)_2PS\}_2][AlCl_4]_2$

S–P	2.109(2)	S–P′	2.083(2)
P–N(1)	1.601(5)	P–N(2)	1.607(5)
N(1)–C(1)	1.497(8)	N(1)–C(3)	1.482(8)
N(2)–C(5)	1.486(8)	N(2)–C(7)	1.458(8)
C(1)–C(2)	1.46(1)	C(3)–C(4)	1.51(1)
C(5)–C(6)	1.48(1)	C(7)–C(8)	1.49(1)
Al–Cl(1)	2.134(3)	Al–Cl(2)	2.109(4)
Al–Cl(3)	2.126(3)	Al–Cl(4)	2.113(3)
P–S–P′	84.0(1)	S–P–S′	96.0(1)
S–P–N(1)	113.1(2)	S–P–N(2)	108.8(2)
N(1)–P–N(2)	112.0(3)	P–N(1)–C(1)	125.5(5)
P–N(1)–C(3)	117.5(4)	C(1)–N(1)–C(3)	117.0(5)
P–N(2)–C(5)	119.6(5)	P–N(2)–C(7)	123.9(5)
C(5)–N(2)–C(7)	115.6(6)	N(1)–C(1)–C(2)	113.3(7)
N(1)–C(3)–C(4)	112.2(7)	N(2)–C(5)–C(6)	112.8(7)
N(2)–C(7)–C(8)	112.3(7)	Cl(1)–Al–Cl(2)	110.3(2)
Cl(1)–Al–Cl(3)	109.5(1)	Cl(2)–Al–Cl(3)	108.1(1)
Cl(1)–Al–Cl(4)	109.2(1)	Cl(2)–Al–Cl(4)	109.6(2)
Cl(3)–Al–Cl(4)	110.1(2)		

Table 7. Bond distances (Å) and angles (°) for $[\{(Et_2N)_2PSe\}_2][AlCl_4]_2$

Se(1)–P(1)	2.257(3)	Se(1)–P(2)	2.238(3)
Se(2)–P(1)	2.249(3)	Se(2)–P(2)	2.262(3)
P(1)–N(1)	1.614(9)	P(1)–N(2)	1.58(1)
P(2)–N(3)	1.60(1)	P(2)–N(4)	1.625(9)
N(1)–C(1)	1.50(2)	N(1)–C(3)	1.42(1)
N(2)–C(5)	1.51(1)	N(2)–C(7)	1.45(2)
N(3)–C(9)	1.49(1)	N(3)–C(11)	1.49(1)
N(4)–C(13)	1.48(1)	N(4)–C(15)	1.50(1)
C(1)–C(2)	1.49(2)	C(3)–C(4)	1.47(2)
C(5)–C(6)	1.43(2)	C(7)–C(8)	1.47(2)
C(9)–C(10)	1.49(2)	C(11)–C(12)	1.54(2)
C(13)–C(14)	1.48(2)	C(15)–C(16)	1.52(1)
Al(1)–Cl(1)	2.132(5)	Al(1)–Cl(2)	2.103(6)
Al(1)–Cl(3)	2.099(6)	Al(1)–Cl(4)	2.113(6)
Al(2)–Cl(5)	2.124(5)	Al(2)–Cl(6)	2.079(5)
Al(2)–Cl(7)	2.146(6)	Al(2)–Cl(8)	2.098(5)
P(1)–Se(1)–P(2)	82.9(1)	P(1)–Se(2)–P(2)	82.6(1)
Se(1)–P(1)–Se(2)	97.2(1)	Se(1)–P(1)–N(1)	118.0(4)
Se(2)–P(1)–N(1)	110.1(4)	Se(1)–P(1)–N(2)	109.4(4)
Se(2)–P(1)–N(2)	113.2(4)	N(1)–P(1)–N(2)	108.7(5)
Se(1)–P(2)–Se(2)	97.3(1)	Se(1)–P(2)–N(3)	110.2(4)
Se(2)–P(2)–N(3)	112.9(4)	Se(1)–P(2)–N(4)	116.1(4)
Se(2)–P(2)–N(4)	108.7(4)	N(3)–P(2)–N(4)	111.0(5)
P(1)–N(1)–C(1)	118.6(9)	P(1)–N(1)–C(3)	125.4(9)
C(1)–N(1)–C(3)	114(1)	P(1)–N(2)–C(5)	125.8(9)
P(1)–N(2)–C(7)	119.2(9)	C(5)–N(2)–C(7)	114(1)
P(2)–N(3)–C(9)	125.8(8)	P(2)–N(3)–C(11)	116.9(8)
C(9)–N(3)–C(11)	117(1)	P(2)–N(4)–C(13)	118.6(8)
P(2)–N(4)–C(15)	122.2(8)	C(13)–N(4)–C(15)	117.7(9)
N(1)–C(1)–C(2)	114(2)	N(1)–C(3)–C(4)	118(1)
N(2)–C(5)–C(6)	114(1)	N(2)–C(7)–C(8)	119(1)
N(3)–C(9)–C(10)	111(1)	N(3)–C(11)–C(12)	116(1)
N(4)–C(13)–C(14)	112(1)	N(4)–C(15)–C(16)	112(1)
Cl(1)–Al(1)–Cl(2)	109.6(2)	Cl(1)–Al(1)–Cl(3)	107.7(3)
Cl(2)–Al(1)–Cl(3)	110.2(3)	Cl(1)–Al(1)–Cl(4)	108.8(3)
Cl(2)–Al(1)–Cl(4)	109.6(3)	Cl(3)–Al(1)–Cl(4)	110.8(3)
Cl(5)–Al(2)–Cl(6)	111.3(2)	Cl(5)–Al(2)–Cl(7)	108.0(2)
Cl(6)–Al(2)–Cl(7)	108.3(2)	Cl(5)–Al(2)–Cl(8)	108.2(2)
Cl(6)–Al(2)–Cl(8)	111.0(3)	Cl(7)–Al(2)–Cl(8)	110.0(3)

Table 8. Bond distances (Å) and angles (°) for $(\mathrm{Pr^i{}_2N})_2\mathrm{P(Cl)S{\cdot}AlCl_3}$

P–S	2.017(6)	P–Cl(1)	1.987(6)
P–N(1)	1.64(1)	P–N(2)	1.64(1)
S–Al	2.291(7)	Al–Cl(2)	2.110(7)
Al–Cl(3)	2.100(7)	Al–Cl(4)	2.123(7)
N(1)–C(1)	1.52(2)	N(1)–C(4)	1.49(2)
N(2)–C(7)	1.50(2)	N(2)–C(10)	1.47(2)
C(1)–C(2)	1.54(2)	C(1)–C(3)	1.49(2)
C(4)–C(5)	1.48(2)	C(4)–C(6)	1.54(2)
C(7)–C(8)	1.55(2)	C(7)–C(9)	1.52(2)
C(10)–C(11)	1.52(2)	C(10)–C(12)	1.51(2)
S–P–Cl(1)	109.8(3)	S–P–N(1)	108.5(5)
Cl(1)–P–N(1)	110.3(5)	S–P–N(2)	112.7(5)
Cl(1)–P–N(2)	106.3(5)	N(1)–P–N(2)	109.3(6)
P–S–Al	112.2(2)	S–Al–Cl(2)	109.5(3)
S–Al–Cl(3)	115.6(3)	Cl(2)–Al–Cl(3)	111.2(3)
S–Al–Cl(4)	98.2(3)	Cl(2)–Al–Cl(4)	111.3(3)
Cl(3)–Al–Cl(4)	110.4(3)	P–N(1)–C(1)	118(1)
P–N(1)–C(4)	124(1)	C(1)–N(1)–C(4)	115(1)
P–N(2)–C(7)	113.3(9)	P–N(2)–C(10)	129(1)
C(7)–N(2)–C(10)	116(1)	N(1)–C(1)–C(2)	110(1)
N(1)–C(1)–C(3)	110(1)	C(2)–C(1)–C(3)	115(2)
N(1)–C(4)–C(5)	119(2)	N(1)–C(4)–C(6)	111(2)
C(5)–C(4)–C(6)	112(1)	N(2)–C(7)–C(8)	111(1)
N(2)–C(7)–C(9)	110(1)	C(8)–C(7)–C(9)	112(1)
N(2)–C(10)–C(11)	113(2)	N(2)–C(10)–C(12)	114(1)
C(11)–C(10)–C(12)	115(2)		

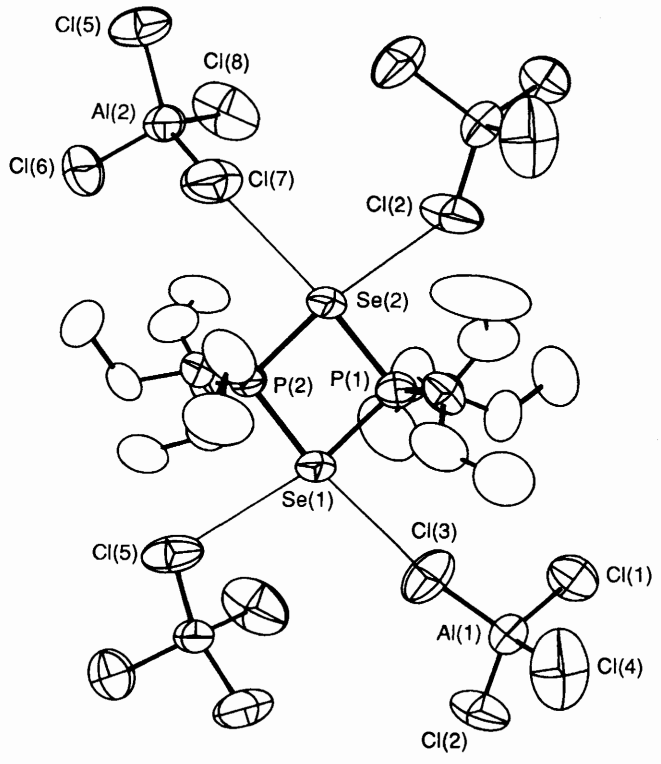


Figure 2. View of the cation $[\{(\mathrm{Et_2N})_2\mathrm{PSe}\}_2]^{2+}$ showing the contacts with the $\mathrm{AlCl_4}^-$ units

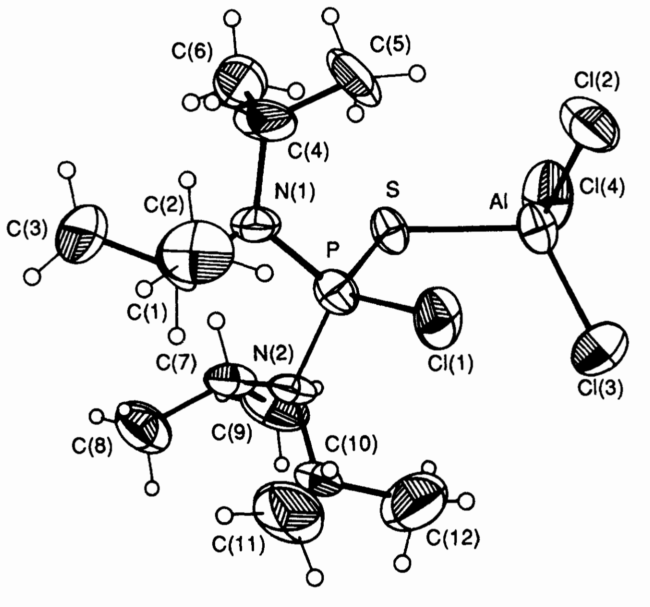
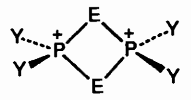
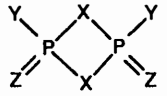


Figure 3. View of $(\mathrm{Pr^i{}_2N})_2\mathrm{P(Cl)S{\cdot}AlCl_3}$



(3)

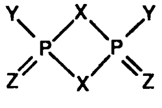


(4)

I.r. Spectroscopic Characterisation. Comparison of the i.r. spectra for the three derivatives of $(\mathrm{R_2N})_2\mathrm{P(S)Cl}$ (R = Me,[17] Et, or Pr$^\mathrm{i}$) and of $(\mathrm{R_2N})_2\mathrm{P(Se)Cl}$, (R = Me,[9] Et, or Pr$^\mathrm{i}$) provides support for the assignments of P–S and P–Se stretching frequencies, which can be monitored following their reaction with $\mathrm{AlCl_3}$. Two bands (R = Me, 605, 735; R = Et, 610, 735; R = Pr$^\mathrm{i}$, 595, 705 cm^{-1}) are assigned to P–Se stretching frequencies (550—730 cm^{-1} and 658—802 cm^{-1}),[18] and these are the only bands which occur at lower wavenumber for the respective P–Se stretches in the selenium derivatives (R = Me, 550, 700; R = Et, 555, 685; R = Pr$^\mathrm{i}$, 565, 640 cm^{-1}). These bands are not present in the spectra of the Me/S, Et/S, Me/Se, and Et/Se derivatives of $\mathrm{R_4N_2PEAlCl_4}$ in the solid state. Moreover, one of the bands shifts to lower wavenumber in the spectra of $(\mathrm{Pr^i{}_2N})_2\mathrm{P(Cl)S{\cdot}AlCl_3}$ (595, 640 cm^{-1}) and $(\mathrm{Pr^i{}_2N})_2\mathrm{P(Cl)S{\cdot}GaCl_3}$ (595, 645 cm^{-1}), implying a slight weakening of the P–S bond upon complex formation.[19] The i.r. spectrum of $(\mathrm{Pr^i{}_2N})_2\mathrm{P(Cl)S{\cdot}AlCl_3}$ is identical to that of $(\mathrm{Pr^i{}_2N})_2\mathrm{P(Cl)S{\cdot}GaCl_3}$ above 550 cm^{-1}, and to that of $\mathrm{Ph_3PS{\cdot}AlCl_3}$ below 650 cm^{-1}.[19] These observations confirm the co-ordination complex structures and allow tentative assignment of the bands in these regions. The ionic nature of the Me/S, Et/S, Me/Se, and Et/Se derivatives of $\mathrm{R_4N_2PEAlCl_4}$ in the solid state, is demonstrated by the presence of the strong broad band centred at 485 cm^{-1} in the i.r. spectra, characteristic of $\mathrm{AlCl_4}^-$.[20]

Crystal Structures of $[\{(\mathrm{Et_2N})_2\mathrm{PS}\}_2][\mathrm{AlCl_4}]_2$ *and* $[\{(\mathrm{Et_2N})_2\mathrm{PSe}\}_2][\mathrm{AlCl_4}]_2$.—While the compounds are not isostructural, they have very similar structural features (Figures 1 and 2). Both crystal structures consist of discrete cationic and anionic units, although a number of long interionic contacts are evident. The cation is a dimeric structure consisting of two $(\mathrm{Et_2N})_2\mathrm{PE}^+$ fragments bound together as a $\mathrm{P_2E_2}$ four-membered ring. The heterocycle is planar by symmetry for the thio derivative and the maximum deviation from planarity for the seleno derivative is 0.003 Å, and the plane is perpendicular to the plane of the four amino substituent centres. Distorted tetrahedral geometries are observed at phosphorus, enforced by the four-membered framework. The amine units ($\mathrm{C_2NP}$) are individually planar with short P–N bond lengths [E = S, 1.601(5), 1.607(5) Å; E = Se, 1.614(9), 1.60(1), 1.58(1), 1.625(9) Å; *cf.*, P–N single bond 1.77 Å],[21] indicating the presence of substantial P–N π

Table 9. Structural parameters and ^{31}P n.m.r. chemical shifts for dichalcogenadiphosphetanes (**4**)



(**4**)

X	Y	Z	P–X/Å	XPX/°	PXP/°	δ(^{31}P)/p.p.m.	Ref.
S	NEt_2	NEt_2	2.083(2)	96.0(1)	84.0(1)	21	This work
S	Me	S	2.141(6)	94.54(22)	85.46(23)		*a*
S	Ph	S	2.108(2) 2.133(2)	93.1(1)	86.9(1)	15	*b*
S	Mesityl	S	2.093(1) 2.125(1) 2.125(1)	93.8(1)	86.2(1)	11	*c*
S	NMe_2	S	2.122(1)	93.14(3)	86.86(3)	24	*d*
S	$N(SiMe_3)_2$	NBu^t	2.160(1)	90.35(4)	89.20(4)		*e*
S	S^- (Zn^{2+})	S	2.117(3) 2.124(3) 2.125(3) 2.110(3)	94.0(1) 94.2(1)	86.0(1) 85.8(1)		*f*
S	S^- (Ag^+)	S	2.120(2)	93.71(8)	86.29(8)		*g*
Se	NEt_2	NEt_2	2.257(3) 2.238(3) 2.249(3) 2.262(3)	97.2(1) 97.3(1)	82.9(1) 82.6(1)	−7.8	This work
Se	Bu^t	Se	2.269(2)	96.5(1)	83.5(1)		*h*
Se	Ph	R^i	2.277(2) 2.259(2)	95.3(1)	83.5(1)		*j*

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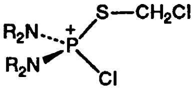
interaction. A similar shortening is observed for other aminophosphonium centres.[22] The P–S bond lengths [2.109(2), 2.083(2) Å] are slightly shorter than a P–S single bond [$(PhS)_3P$, 2.122(8) Å;[23] P_4S_{10}, 2.097 Å [21]]; however, the P–Se bonds [2.257(3), 2.249(3), 2.238(3), 2.262(3) Å] are typical of single bonds (P_4Se_3, 2.24 Å).[21]

Consequently, the overall molecular bonding is best viewed as resonance structures involving a delocalisation of the positive charge onto the amine centres. On this basis, derivatives of (**3**) have an isovalent relationship to numerous derivatives of the dichalcogenadiphosphetanes (**4**).[24] However, there are important structural differences worthy of note, as illustrated in Table 9. In general, the endocyclic bonds of the thio derivatives of (**3**) are shorter than the single bond lengths observed universally for the dithiadiphosphetanes. The angle at phosphorus is substantially wider, while the angle at sulphur is significantly narrower. Similar trends are observed for the angles of the seleno derivative by comparison with diselenadiphosphetanes, although the P–Se bond lengths are essentially indistinguishable.

The slight distortion of the P_2E_2 ring observed in the cations in comparison to the neutral phosphetanes, may be a function of the phosphonium character at the phosphorus centres. In addition, the influence of interactions between the cations and the anions is significant. Two long contacts exist between each chalcogen centre of the cation and the chlorine centres of the anions. While the S–Cl distances [S–Cl(1) = 3.591(3), S–Cl(3) = 3.368(3) Å] are within the sum of the van der Waal's radii (3.70 Å), the Se–Cl interactions are substantially shorter [Se(1)–Cl(3) = 3.211(4), Se(1)–Cl(5) = 3.438(5), Se(2)–Cl(2) = 3.499(6), Se(2)–Cl(7) = 3.462(4) Å; van der Waals radii, 3.80 Å]. As illustrated in Figures 1 and 2, one $AlCl_4^-$ unit is associated with each sulphur centre forming two contacts in a chelate fashion, while the chlorine centres of two different anions are associated with each selenium centre. Moreover, the observed distortions from tetrahedral geometry of the anions, evident in both bond lengths and bond angles, are consistently more pronounced in the selenium system. Contacts of this nature are common for non-metal cations[25,6a,6e] and are interpreted as donations from the anion to the cation.[26] While the structural features of the cation imply localisation of the molecular charge in the P–N region, steric restrictions prevent the approach of the anion to these areas. Consistently, the contacts are specific to a single chalcogen centre, unlike many less sterically shielded non-metal cationic systems, which display bridging contacts over two bound centres.[25,6a,6b] Moreover, the interactions occur in the P_2E_2 plane. For E = S, the maximum deviation of any atom from the mean plane defined by P, S, Cl(1), Cl(3), P′, S′, Cl(1′), and Cl(3′) is 0.23 Å. Alternatively, the P, S, P′, S′, and S, Cl(1), Cl(3) planes intersect at only 15.6°. Similarly, for E = Se, the maximum deviation from planarity is 0.52 Å and the average dihedral angle is 8.5°. Therefore, the conformations of the cation–anion interactions appear to be defined by steric factors.

Crystal Structure of $(Pr^i_2N)_2P(Cl)S\cdot AlCl_3$.—In contrast to the ionic structures (**3**) observed for the Et/S and Et/Se derivatives of $R_4N_2PEAlCl_4$, the discrete molecular units consist of a $(Pr^i_2N)_2P(Cl)S$ unit co-ordinated to $AlCl_3$ *via* the sulphur centre as in (**2**). The Al–S bond length [2.291(7) Å] is identical to that in $Ph_3PS{\cdot}AlCl_3$ [Al–S, 2.297(2); P–S, 2.028(2) Å],[2b] as is the P–S bond length [2.017(6) Å]. The nitrogen centres are typically planar, indicative of a π interaction with the phosphorus centre, and the P–N bond lengths [1.64(1) Å] are similar to those of the dications $[\{(Et_2N)_2PE\}_2]^{2+}$ [E = S, 1.601(5), 1.607(5); E = Se, 1.614(9), 1.58(1), 1.60(1), 1.625(9) Å]. Figure 3 illustrates the steric presence of the isopropyl groups. The short P–Cl bond [1.987(6) Å; *cf.*, PCl_5, 2.124(3), 2.020(3) Å] [20] implies a degree of π bonding, as observed in the free base.[27] This chlorine atom [Cl(1)] has a contact [3.581(7) Å] with the aluminium centre, which is probably a function of the spatial requirements of the structure rather than a bonding interaction. The $AlCl_3$ moiety is distorted [S–Al–Cl(2), 109.5(3); S–Al–Cl(3), 115.6(3); S–Al–Cl(4), 98.2(3)°] in such a way as to tilt the chlorine centres away from the phosphorus centre, and the Al–P contact distance [3.579(6) Å] is slightly shorter than those in $Ph_3PS{\cdot}AlCl_3$ and $Ph_3PSe{\cdot}AlCl_3$.[2b] In this context, we view the structure as an example of $P{=}S{\rightarrow}Al$ π complexation, using the 'organometallic' terminology.[2b] However, the P–S–Al angle [112.2(2)°] is slightly larger than that in $Ph_3PS{\cdot}AlCl_3$ [109.62(8)°].

Reaction Between $(R_2N)_2P(Cl)S{\cdot}AlCl_3$ *and* CH_2Cl_2.—Solutions of $(R_2N)_2P(Cl)S{\cdot}AlCl_3$ in CH_2Cl_2 heated to 80 °C undergo quantitative reactions to give ionic systems, which have been characterised by ^{13}C, ^{31}P (Table 1), and ^{27}Al n.m.r. spectroscopy. The process also occurs slowly at room temperature (fastest for R = Pr^i), and is irreversible. On a preparative scale, a mass-balance experiment (R = Pr^i) shows a molecular weight increase corresponding to an equimolar reaction between the adduct and CH_2Cl_2. The identity of the cations as derivatives of (5) is demonstrated by a triplet signal (not present in the spectra of the corresponding adducts) in the ^1H coupled ^{13}C n.m.r. spectra between 44 and 46 p.p.m., which is typical of a methylene group attached to sulphur.[28] On this basis, the process is rationalised as an acid induced electrophilic attack of the sulphur centre by the solvent, resulting in a chloride ion abstraction from the solvent to form $AlCl_4^-$. A similar reaction is observed for $Ph_3PS{\cdot}AlCl_3$, but not for $(Me_2N)_3PS{\cdot}AlCl_3$.[29]



(5)

Chalcogenophosphonium Cations in Solution.—Derivatives of (3) dissolve in CH_2Cl_2 and provide n.m.r. spectra which are identical to those of the reaction mixtures of the phosphinic halides with $AlCl_3$. The Et/Se derivative, $[\{(Et_2N)_2PSe\}_2][AlCl_4]_2$, is observed as a component of a complex equilibrium in solution. While the Me/Se derivative, $[\{(Me_2N)_2PSe\}_2][AlCl_4]_2$, is believed to have similar behaviour, the low solubility of this system has precluded comprehensive solution studies. In contrast, the sulphur derivatives favour the covalent adduct structures in solution. However, the Et/S derivative $[\{(Et_2N)_2PS\}_2][AlCl_4]_2$ has been observed during the solvation process by means of ^{31}P n.m.r. (Et/S, 21 p.p.m.), and is assigned by comparison with other phosphetane systems (Table 9) and on the basis of the ^{27}Al n.m.r. spectrum ($AlCl_4^-$). Interestingly, the presence of excess $AlCl_3$ enhances the formation of (or stabilises) the dicationic species in solution, and the Me/S (27 p.p.m.) and Pr^i/S (18 p.p.m.) derivatives have been identified in solution, by ^{31}P n.m.r. Unfortunately, these solutions are unstable, as the reaction with the solvent is also enhanced resulting in the formation of compound (5) (see above). The role of $AlCl_3$ in adjustment of the equilibrium may involve activation of the phosphoryl system towards dimerisation, and heterocyclic formation prior to halide ion abstraction. Nevertheless, the observation of the dication for the Pr^i/S system in solution, despite the solid-state structure, demonstrates the thermodynamic preference for the dication, and indicates a kinetic stabilisation of the complex $(Pr^i_2N)_2P(Cl)S{\cdot}AlCl_3$, possibly by virtue of steric influences.

Conclusion

The diaminochalcogenophosphinic halide–aluminium trichloride system involves two molecular arrangements which are energetically similar, but structurally and electronically very different. The formation of a covalent Lewis acid–base complex is confirmed conclusively for the sulphur derivatives, both in solution and in the solid state for the Pr^i_2N derivative. However, the thermodynamically preferred arrangement, for both the thio- and seleno-derivatives, is a novel dimeric dicationic heterocycle.

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