Covalent Alternatives for the Elusive Iminophosphonium Cation. Crystal Structures of PCl(NPr$^i_2$)$_2$NPh·AlCl$_3$ and P(NPr$^i_2$)$_2$[NPh(SO$_2$CF$_3$)]O §

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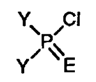
Reactions between diaminoiminophosphinic chlorides and the chloride-abstracting agents AlCl$_3$ and Ag(SO$_3$CF$_3$) have been comprehensively examined as potential routes to the three-co-ordinate iminophosphonium cation. However, bis(dialkylamino)(phenylimino)phosphinic chlorides react to give the covalent phosphoryl systems PCl(NR$_2$)$_2$NPh·AlCl$_3$ and P(NR$_2$)$_2$[NPh(SO$_2$CF$_3$)]O respectively, in quantitative yield. The AlCl$_3$ complexes are also prepared quantitatively from the reaction of P(NPr$^i_2$)$_2$$^+$AlCl$_4^-$ with PhN$_3$ (Staudinger reaction). All compounds have been comprehensively characterised and the structures of the isopropyl derivatives confirmed by X-ray crystallography. Crystal data: PCl(NPr$^i_2$)$_2$NPh·AlCl$_3$, space group $P2_1$, a = 8.719(2), b = 15.553(2), c = 9.509(2) Å, β = 102.73(2)°, Z = 2, R = 0.029; P(NPr$^i_2$)$_2$[NPh(SO$_2$CF$_3$)]O, space group $P2_1/n$, a = 10.594(3), b = 13.222(2), c = 17.084(3) Å, β = 97.71(2)°, Z = 4, R = 0.048. The results indicate that the three-co-ordinate diaminoiminophosphonium cation is thermodynamically unstable with respect to the observed alternative covalent structures, and that steric shielding is responsible for the stability of the analogous diaminomethylenephosphonium cation.

We have begun a programme into the synthesis of low co-ordinate phosphonium centres which are analogues of the alkenic, alkynic and allenic environments for carbon, and therefore represent important keys in the development of pnicogen chemistry. The first structurally characterised example of such a centre is the three-co-ordinate methylenephosphonium centre **2b** [E = C(SiMe$_3$)$_2$, Y = NPr$^i_2$], recently reported by Bertrand and co-workers.[1] In 1982 Sanchez and co-workers[2a] recognised the chlorophosphoryl unit **1** (E = NR or S) as a potential precursor to the alkenic phosphonium centre and reported a solution identification of imino-derivatives (E = NR) of **2a**. However, more recent studies by Chernega *et al.*[3] and this laboratory[4,5] reveal alternative structural arrangements for the cationic imino-[3] and chalcogeno-[4,5]phosphoryl unit. Therefore, we have now performed a comprehensive investigation into the PCl(NR$_2$)$_2$NPh–AlCl$_3$ and –Ag(SO$_3$CF$_3$) systems (R = Et or Pr^i). The spectroscopic and structural data conclusively demonstrate the covalent nature of these systems, and provide a better understanding of the stability of the rare three-co-ordinate phosphonium centre **2**.



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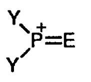

2a E = NPh
2b E = C(SiMe$_3$)$_2$

Experimental

General Procedures.—Phenyl azide (20%, hexane solution, Pfaltz and Bauer) and Ag(SO$_3$CF$_3$) (Aldrich) were obtained commercially and used without purification. Anhydrous AlCl$_3$ (Aldrich) was sublimed under vacuum before use. Dichloromethane and hexane were dried over P$_2$O$_5$ and CaH$_2$ and stored in evacuated bulbs, CD$_2$Cl$_2$ and CDCl$_3$ were dried over P$_2$O$_5$ and CD$_2$Cl$_2$ was stored over [P(NEt$_2$)$_2$Se]$_2$[AlCl$_4$]$_2$.[4] The compounds PCl(NEt$_2$)$_2$[6] and PCl(NPr$^i_2$)$_2$[7] were prepared by literature methods and characterised by NMR spectroscopy, PCl(NEt$_2$)$_2$NPh by reaction of PCl(NEt$_2$)$_2$ with PhN$_3$ in hexane and characterised similarly. Solids were manipulated in a Vacuum/Atmosphere nitrogen-filled glove-box. Glass equipment was flame dried before use. Reactions were performed in an evacuated (10^{-3} Torr, *ca.* 0.133 Pa) dual-compartment vessel, a modification of that described earlier.[8] Melting points were recorded on a Fisher-Johns apparatus and are uncorrected. Elemental analyses were performed by Beller Laboratories, Göttingen. Infrared spectra were recorded as Nujol mulls on CsI plates using a Perkin-Elmer 283B spectrophotometer, NMR spectra on a Nicolet NT-360 spectrometer in 5 and 10 mm flame-sealed Pyrex tubes. Chemical shifts are reported in ppm relative to external standards, 85% H$_3$PO$_4$ for ^{31}P and [Al(H$_2$O)$_6$]$^{3+}$ for ^{27}Al, and relative to the solvent signal for ^{1}H and ^{13}C. *i*, *o*, *m* and *p* refer to the *ipso*, *ortho*, *meta* and *para* carbon atoms respectively. Mass spectra were obtained using a CEC model 21-104 mass spectrometer.

Preparation of PCl(NPr$^i_2$)$_2$NPh.—A solution of PhN$_3$ (1.73 g, 14.6 mmol) in CH$_2$Cl$_2$ (10 cm^3) was added to a solution of PCl(NPr$^i_2$)$_2$ (3.52 g, 13.2 mmol) in CH$_2$Cl$_2$ (11 cm^3) and the reaction mixture was heated to 95 °C for 48 h. The volatiles were removed to give a solid, which was purified by double vacuum sublimation at 115 °C and recrystallisation from warm hexane to give a large single colourless crystal, characterised as bis(diisopropylamino)(phenylimino)phosphinic chloride, yield 0.48 g, 1.3 mmol (10%), m.p. 86 °C. Mass spectrum [m/z (relative intensity)]: 357 (26), 322 (22), 314 (68), 166 (74) and 100 (100). NMR: ^{31}P, δ −8; ^{13}C, δ 147.4 (*i*), 128.5 (*m*), 122.4 (J_{PC} = 20.1 Hz) (*o*), 118 (*p*), 47.5, 22.5 and 22.2. IR: 1600s, 1505s, 1200s, 1175s, 1160(sh), 1125s, 1095m, 1070w, 1015m, 990s,

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† For correspondence regarding chemistry.

‡ For correspondence regarding crystallography.

§ Bis(diisopropylamino)(phenylimino)phosphinic chloride–aluminium trichloride (1/1) and bis(diisopropylamino)[phenyl(trifluoromethylsulphonyl)amino]phosphine oxide.

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, pp. xviii–xxii.

970(sh), 885m, 850w, 750s, 690s, 665m, 615m, 560(sh), 540s, 505(sh), 450w, 410w and 385w cm^{-1}.

A second crop of crystals (2.20 g; total yield 2.68 g, 7.46 mmol, 57%) was obtained from the hexane solution. The compound is air sensitive, and hydrolyses slowly over several months in the solid state.

Preparation and Isolation of PCl(NR$_2$)$_2$NPh·AlCl$_3$ (R = Et *or* Pr^i) *Complexes.*—A solution of P(NR$_2$)$_2$$^+$AlCl$_4$$^-$ was prepared[9] *in situ* by the reaction of PCl(NR$_2$)$_2$ (R = Et, 1.31 g, 6.22 mmol; Pr^i, 2.42 g, 9.08 mmol) with AlCl$_3$ (R = Et, 0.83 g, 6.22 mmol; Pr^i, 1.21 g, 9.08 mmol) in CH$_2$Cl$_2$ (R = Et, 38 g; Pr^i, 46 g). Upon solvation of AlCl$_3$ the solution was cooled to −78 °C and a solution of phenyl azide (R = Et, 0.74 g, 6.22 mmol; Pr^i, 1.08 g, 9.08 mmol) in CH$_2$Cl$_2$ (R = Et, 13 g; Pr^i, 23 g) was added in small aliquots. Evolution of N$_2$ began as the solution warmed to room temperature and the reaction was complete after stirring for several hours at room temperature. The coloured solutions (R = Et, yellow; Pr^i, orange) were degassed, two thirds of the CH$_2$Cl$_2$ was removed and hexane (5 cm^3) was added. Slow removal of solvent yielded a crystalline solid, which was recrystallised by slow cooling of the warm (55 °C) solvent mixture, to give large transparent crystals. The crystals were characterised as bis(dialkylamino)(phenylimino)phosphinic chloride–trichloroaluminium.

R = Et: yield 1.11 g, 2.55 mmol (41%), m.p. 163–165 °C. Mass spectrum [*m*/*z* (relative intensity)]: 301 (27), 266 (12), 229 (19), 194 (13) and 138 (100). NMR: ^{31}P, δ 48.5; ^{13}C, δ 141.2 (*i*), 129.7 (*m*), 129.3 (*o*), 127.1 (*p*), 40.5 and 12.1; ^{27}Al, δ 100 (linewidth at half height $\Delta\nu_{\frac{1}{2}}$ = 132 Hz). IR: 1595m, 1490(sh), 1340(sh), 1285w, 1200s, 1150s, 1115w, 1095w, 1075w, 1040s, 1020s, 975w, 950w, 920w, 910w, 850s, 810m, 795m, 765m, 710w, 695m, 680m, 625m, 565s, 525(sh), 500s, 490s, 460(sh), 435w and 400s cm^{-1} (Found: C, 38.70; H, 5.90; N, 9.55; P, 7.00. Calc. for C$_{14}$H$_{25}$AlCl$_4$N$_3$P: C, 38.65; H, 5.80; N, 9.65; P, 7.10%).

R = Pr^i: yield 0.953 g, 1.94 mmol (21%), m.p. 179 °C. Mass spectrum [*m*/*z* (relative intensity)]: 357 (10), 314 (40), 271 (12), 257 (14), 166 (62), 157 (11), 137 (19), 122 (45) and 100 (100). NMR: ^{31}P, δ 51; ^{13}C, δ 140.4 (*i*), 130.9 (*m*), 129.6 (*o*), 127.4 (*p*), 51.1, 24.4 and 23.6; ^{27}Al, δ 100 ($\Delta\nu_{\frac{1}{2}}$ = 122 Hz). IR: 1595m, 1410(sh), 1305w, 1210s, 1165(sh), 1150s, 1125(sh), 1075w, 1035(sh), 1015s, 980(sh), 885w, 870w, 840s, 830(sh), 755w, 695s, 655m, 640s, 570s, 555m, 530(sh), 485s, 440w, 425w and 395m cm^{-1} (Found: C, 44.00; H, 6.85; N, 8.55. Calc. for C$_{18}$H$_{33}$AlCl$_4$N$_3$P: C, 44.00; H, 6.75; N, 8.55%).

The isolated yields are not optimised. Phosphorus-31 NMR studies of these reaction mixtures and those of the free base iminophosphinic chlorides with AlCl$_3$ [PCl(NR$_2$)$_2$NPh: R = Et, 0.11 g, 0.37 mmol; Pr^i, 0.11 g, 0.30 mmol. CH$_2$Cl$_2$: R = Et, 4 g; Pr^i, 3.1 g. AlCl$_3$: R = Et, 0.05 g, 0.37 mmol; Pr^i, 0.04 g, 0.30 mmol] showed essentially quantitative formation of the PCl(NR$_2$)$_2$NPh·AlCl$_3$ complexes. The ^{27}Al NMR spectra show no indication of the presence of AlCl$_4$$^-$ (δ 102, $\Delta\nu_{\frac{1}{2}}$ < 30 Hz).[4] The spectra were unchanged when solutions of PCl(NR$_2$)$_2$NPh·AlCl$_3$ were heated to 60 °C for 24 h.

Exposure of PCl(NR$_2$)$_2$NPh·AlCl$_3$ *Complexes to Air.*—Ground crystals of PCl(NR$_2$)$_2$NPh·AlCl$_3$ (R = Et or Pr^i) were exposed to the air for 10 min. Dissolution of the material in CDCl$_3$ (used as received) left a white precipitate. The solution was examined by NMR spectroscopy, and the only phosphorus-containing species present was tentatively characterised as bis(dialkylamino)(phenylimino)phosphinic hydroxide P(NR$_2$)$_2$(NPh)OH. NMR: ^{31}P, R = Et, δ 39; Pr^i, 35; ^{13}C, R = Et, δ 136.4 (*i*), 129.6 (*m*), 125.1 (*p*), 120.6 (*o*), 41.3 and 13.1; Pr^i, 136.5 (*i*), 129.2 (*m*), 125.2 (*p*), 122.4 (*o*) (J_{PC} = 6.8 Hz), 50.5 and 23.1; ^{1}H, R = Et, δ 9.57 (1 H) (concentration dependent, range 9.5–11.4), 7.3–7.1 (5 H, aromatic), 3.4–3.2 (8 H, dq) and 1.3 (12 H, t, J_{HH} = 7.2); Pr^i, 11.45 (1 H, d, J_{HP} = 14) (concentration dependent), 7.5–7.0 (5 H, aromatic), 4.1–4.0 (4 H, m), 1.59 (12 H, d, J_{HH} = 6.9) and 1.47 (12 H, d, J_{HH} = 6.8 Hz). These compounds could not be isolated. A small amount of aluminium was present in the solution as AlCl$_4$$^-$: ^{27}Al, δ 102 ($\Delta\nu_{\frac{1}{2}}$ < 30 Hz).

Reaction of PCl(NPr^i$_2$)$_2$NPh *with* Ag(SO$_3$CF$_3$). *Preparation and Isolation of* P(NPr^i$_2$)$_2$[NPh(SO$_2$CF$_3$)]O.—A solution of PCl(NPr^i$_2$)$_2$NPh (0.743 g, 2.08 mmol) in CH$_2$Cl$_2$ (20 cm^3) was added to Ag(SO$_3$CF$_3$) (0.534 g, 2.08 mmol). Reaction occurred immediately and the solution was stirred overnight. The CH$_2$Cl$_2$ was removed, hexane (20 cm^3) was added, and the resulting pale yellow solution was decanted from the white precipitate. Slow removal of the solvent yielded an off-white air-stable solid, which was recrystallised six times from hexane and characterised as bis(diisopropylamino)[phenyl(trifluoromethylsulphonyl)amino]phosphine oxide, yield 0.343 g, 0.73 mmol (35%), m.p. 117–118 °C. Mass spectrum [*m*/*z* (relative intensity)]: 471 (1) and 247 (100). NMR: ^{31}P, δ 13; ^{13}C, δ 136.4 (*i*), 131.9 (*m*), 129.9 (*p*), 129.6 (*o*), 120.3 ($^1J_{CF}$ = 325 Hz), 48.7, 23.6 and 23.0. IR: 1600w, 1255s, 1225w, 1200s, 1170w, 1130m, 1070w, 1020s, 970s, 940s, 915m, 880s, 870(sh), 705s, 680s, 620m, 605s, 580m, 565(sh), 550s, 525s, 445m, 405w and 385w cm^{-1} (Found: C, 48.45; H, 7.15; N, 9.00. Calc. for C$_{19}$H$_{33}$F$_3$N$_3$O$_3$PS: C, 48.40; H, 7.05; N, 8.90%).

NMR studies on the reaction mixture show the reaction to be quantitative. Similarly, reactions of PCl(NEt$_2$)$_2$NPh with excess of Ag(SO$_3$CF$_3$) gave a single product (^{31}P, δ 14).

Reaction of P(NPr^i$_2$)$_2$$^+SO_3CF_3$$^-$ *with Phenyl Azide.*—The azide (2.08 mmol) in CH$_2$Cl$_2$ (10 cm^3) was added to a stirred solution of P(NPr^i$_2$)$_2$$^+SO_3CF_3$$^-$ [prepared *in situ*, 2.09 mmol Ag(SO$_3$CF$_3$), 2.08 mmol PCl(NPr^i$_2$)$_2$] in CH$_2$Cl$_2$ (20 cm^3). A ^{31}P NMR spectrum of the reaction mixture revealed P(NPr^i$_2$)$_2$[NPh(SO$_2$CF$_3$)]O to be the principal (>80%) component; P(NPr^i$_2$)$_2$$^+$ and PCl(NPr^i$_2$)$_2$ were the only other phosphorus-containing species present.

X-Ray Data Collection, Solution and Refinement.—Suitable crystals of P(NPr^i$_2$)$_2$[NPh(SO$_2$CF$_3$)]O (obtained by slow removal of solvent from hexane solutions) were mounted on glass fibres and affixed with epoxy glue. Crystals of PCl(NPr^i$_2$)$_2$NPh·AlCl$_3$ (grown by slow solvent removal under vacuum from a hexane–CH$_2$Cl$_2$ solution) were mounted in thin-walled Pyrex capillaries under an atmosphere of N$_2$ in a dry-box. Unit-cell parameters were obtained from the setting angles of 25 accurately centred reflections having 15 < θ < 18°. The choice of space groups was based on systematically absent reflections and confirmed by the program TRACER[10] and the successful solution and refinement of the structures. The choice of the alternative centric space group $P2_1/m$ for PCl(NPr^i$_2$)$_2$NPh· AlCl$_3$ was eliminated due to the lack of molecular symmetry that would be required. All pertinent crystallographic data are summarised in Table 1.

Data were collected at room temperature on an Enraf-Nonius CAD-4 diffractometer (Mo-Kα, λ = 0.709 30 Å, graphite monochromator) using the ω–2θ scan technique. The stability of the crystals was monitored every 60 min using three standard reflections and no significant decay was observed. Data were corrected for Lorentz and polarisation effects and an empirical absorption correction was applied based on a series of ψ scans. Transmission coefficients are listed in Table 1. Scattering factors were taken from Cromer and Waber[11] and anomalous dispersion effects were included in F_c.[12]

The structures were solved using direct methods[13] to find the heavier elements and the remaining non-hydrogen atoms were located from a series of Fourier difference maps. Hydrogen atoms were included in ideal positions as fixed contributions (B_{iso} = 1.2B of the bonded atom) to the structure factors. The final choice of enantiomer for PCl(NPr^i$_2$)$_2$NPh·AlCl$_3$ was based on a slightly lower R factor (0.0295 *vs.* 0.0297). The model was refined using full-matrix least-squares techniques based on F,

Table 1 Crystal data collection and refinement parameters

Formula	$C_{18}H_{33}AlCl_4N_3P$	$C_{19}H_{33}F_3N_3O_3PS$
M	491.25	471.53
Space group	$P2_1$	$P2_1/n$
Z	2	4
$F(000)$	516	1000
a/Å	8.719(2)	10.594(3)
b/Å	15.553(2)	13.222(2)
c/Å	9.509(2)	17.084(3)
β/°	102.73(2)	97.71(2)
U/Å^3	1257.8	2731.4
Dimensions/mm	0.36 × 0.45 × 0.55	0.33 × 0.38 × 0.50
D_c/g cm^{-3}	1.30	1.32
μ/cm^{-1}	5.8	2.4
Transmission coefficients	0.972–0.999	0.922–1.000
Range of h, k, l	+11, −20, ±12	+12, +15, ±20
$2\theta_{max}$/°	55	50
Reflections measured	3357	4447
Unique	3001	4204
Observed	2643	2585
$[I > 3\sigma(I)]$ parameters	244	271
Goodness of fit[a]	1.11	1.00
R[b]	0.029	0.048
R'[c]	0.030	0.046
Maximum Δ/σ	0.07	0.03
Largest feature in difference map/e Å^{-3}	0.26	0.26

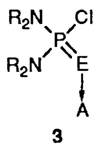
[a] $[\Sigma w(|F_o| - |F_c|)^2/(N_o - N_v)]^{\frac{1}{2}}$ where N_o, N_v = numbers of reflections and parameters. [b] $\Sigma||F_o| - |F_c||/\Sigma|F_o|$. [c] $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma(wF_o)^2]^{\frac{1}{2}}$.

minimising the function $\Sigma w(|F_o| - |F_c|)^2$, where the weight was defined as $w = [\sigma(F)^2 + (0.005F)^2 + 0.4]^{-1}$ in all structures.[14] Positional parameters for non-hydrogen atoms are given in Tables 2 and 3, selected bond lengths and angles in Table 4.

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

Results and Discussion

The Diamino(phenylimino)phosphinic Chloride–Trichloroaluminium System.—Phosphorus-31 NMR studies of reactions between bis(dialkylamino)phosphenium tetrachloroaluminate $[P(NR_2)_2{}^+\ AlCl_4{}^-]$ and phenyl azide, and reactions of bis(dialkylamino)(phenylimino)phosphinic chloride $[PCl(NR_2)_2NPh]$ with $AlCl_3$, show the formation of the covalent Lewis acid-base complex $PCl(NR_2)_2NPh\cdot AlCl_3$ **3** (R = Et or Pr^i, E = NPh), in essentially quantitative yield. The complexes have been isolated as analytically pure crystalline solids. In solution the ^{31}P NMR chemical shifts of the complexes (R = Et, δ 48.5; Pr^i, 51) are deshielded in comparison with the corresponding free bases (R = Et, δ 12; Pr^i, −8). A broad (R = Et, 132; Pr^i, 122 Hz) signal is observed at δ 100 in the ^{27}Al NMR spectra, characteristic of an iminophosphoryl unit bound to $AlCl_3$.[5] In the solid state, a strong to medium IR band is observed for both compounds in the region of 400 cm^{-1}, and can be assigned to the iminophosphoryl–aluminium linkage. The mass spectra do not exhibit a molecular ion, but the base peak corresponds to the free base $PCl(NR_2)_2NPh$, which is typical for phosphoryl–$AlCl_3$ complexes.[4b,5,15] The structure of the complex $PCl(NPr^i_2)_2NPh\cdot AlCl_3$ has been confirmed by X-ray crystallography and a view is shown in Fig. 1. In general, the bond lengths and angles are as might be expected for the units involved.[16a] Interestingly, the *anti* orientation of the phenyl group with respect to the chlorine atom is in contrast to the *gauche* orientation observed for the derivative $PCl(NEt_2)_2NPh\cdot AlCl_3$.[16b] The conformations are likely under the control of steric factors.



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The quantitative formation of the iminophosphoryl–$AlCl_3$ complexes is in contrast to the results of Sanchez and co-workers,[2a] who speculated on the formation of the three-co-ordinate iminophosphonium cation **2a** (Y = NEt_2, ^{31}P NMR δ 37.1) together with the complex $PCl(NEt_2)_2NPh\cdot AlCl_3$ (δ 48.5), in solution. In addition, they suggested that the cation **2a** (observed ^{31}P signal at δ 37.1) is produced quantitatively as a thermolysis product (50 °C) of the $PCl(NEt_2)_2NPh\cdot AlCl_3$ complex.[2a] However, we have discovered that the iminophosphoryl–$AlCl_3$ complexes are thermally stable above 60 °C. More importantly, they are extremely air sensitive (not noted in ref. 2*a*), and minimal air exposure results in hydrolysis to give $P(NR_2)_2(NPh)OH$ which has been spectroscopically characterised (^{31}P NMR: R = Et, δ 39; Pr^i, 35). The ^{13}C NMR spectrum of $P(NEt_2)_2(NPh)OH$ is identical to that reported for cation **2a** (R = Et), as is the ^1H NMR spectrum except for a concentration-dependent signal in the range typical of acidic protons (signal not reported in ref. 2). Hydrolysis reaction mixtures display a sharp signal at δ 102 characteristic of $AlCl_4{}^-$, indicative of the presence of an ionic system. However, $AlCl_4{}^-$ can be detected at very low concentrations,[17] and it is likely that much of the aluminium is contained in the hydrolysis precipitate. The iminophosphinic chlorides $PCl(NR_2)_2NPh$ (R = Et or Pr^i) are themselves hydrolytically unstable, and we observe the ^{31}P NMR signal at δ 39 as an intermediate in the full hydrolysis of $PCl(NEt_2)_2NPh$ to $P(NEt_2)_2(NHPh)O$,[18] in the absence of $AlCl_3$.

The Diamino(phenylimino)phosphinic Chloride–Silver Trifluoromethanesulphonate System.—The compound $PCl(NR_2)_2NPh$ (R = Et or Pr^i) reacts with $Ag(SO_3CF_3)$ in CH_2Cl_2 to give AgCl and $P(NR_2)_2[NPh(SO_2CF_3)]O$ in essentially quantitative yield (^{31}P NMR spectroscopy). The structure of $P(NPr^i_2)_2[NPh(SO_2CF_3)]O$ has been determined by X-ray crystallography,* Fig. 2. Reaction of $P(NPr^i_2)_2{}^+SO_3CF_3{}^-$ with PhN_3 produced the same compound. The ^{31}P NMR chemical shifts of the new triaminophosphoryl centres (R = Et, δ 14; Pr^i, 13) are in the range typical for triaminophosphine oxides[19] [*cf.* $P(NEt_2)_2(NHPh)O$, δ 15]. Furthermore, the IR spectrum (R = Pr^i) exhibits a strong peak at 1255 cm^{-1}, characteristic[20] of the P=O stretching mode and the mass spectrum [m/z 471, parent ion; 247, $P(NPr^i_2)_2O^+$] is consistent with the structure.

The Three-co-ordinate Phosphonium Electronic Environment.—The compounds $PCl(NR_2)_2NPh\cdot AlCl_3$ and $P(NR_2)_2[NPh(SO_2CF_3)]O$ represent two covalent structural alternatives to the alkenic three-co-ordinate iminophosphonium cation **2a**. The structure observed for $P(NPr^i_2)_2[NPh(SO_2CF_3)]O$ **5a** provides a direct comparison with bis(diisopropylamino)[bis(trimethylsilyl)methylene]phosphonium **2b** triflate $[(Pr^i_2N)_2P{=}C(SiMe_3)_2]^+[SO_3CF_3]^-$.[1] Thermodynamic preference for the covalent phosphine oxide alternative **5** (the P=O bond has a very high bond energy, 544 kJ mol^{-1})[21] is manifest in the imino-

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* A feature worthy of note is the P–N(S) bond length [P–N(1) 1.785(3) Å], considerably longer than the other P–N(amino) bonds [P–N(2) 1.649(3) and P–N(3) 1.639(3) Å], and close to a standard P–N single bond (1.78 Å).[16a] The S–N bond [1.628(3) Å] is relatively short demonstrating a preference for N(1) to π-bond with the centre of higher oxidation state and lesser π involvement (sulphur is bound to two oxygen centres, while phosphorus has two nitrogen and one oxygen centre).

Table 2 Positional parameters and their estimated standard deviations (e.s.d.s)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Cl(1)	0.528 26(8)	0.396*	0.683 79(9)	C(6)	1.007 1(4)	0.479 4(3)	0.951 3(4)
Cl(2)	0.866 1(1)	0.693 02(6)	0.656 4(1)	C(7)	0.814 1(4)	0.461 3(2)	0.398 5(3)
Cl(3)	0.507 7(1)	0.597 79(7)	0.539 2(1)	C(8)	0.709 4(5)	0.499 7(3)	0.265 0(4)
Cl(4)	0.660 5(1)	0.621 42(7)	0.910 31(9)	C(9)	0.967 1(4)	0.426 6(3)	0.369 7(4)
P	0.749 70(8)	0.399 39(6)	0.648 32(8)	C(10)	0.625 7(4)	0.327 5(2)	0.395 5(4)
Al	0.714 2(1)	0.596 48(7)	0.706 9(1)	C(11)	0.463 7(4)	0.362 0(3)	0.321 5(5)
N(1)	0.819 4(3)	0.490 1(2)	0.717 7(3)	C(12)	0.699 5(5)	0.277 2(3)	0.289 0(4)
N(2)	0.732 0(3)	0.396 8(2)	0.474 8(2)	C(13)	0.950 0(4)	0.264 7(2)	0.658 9(3)
N(3)	0.835 2(3)	0.313 9(2)	0.726 4(3)	C(14)	0.912 1(5)	0.168 9(2)	0.643 2(4)
C(1)	0.979 1(3)	0.494 0(2)	0.804 3(3)	C(15)	1.121 1(4)	0.280 1(3)	0.730 6(5)
C(2)	1.102 4(4)	0.517 6(2)	0.741 0(4)	C(16)	0.794 5(5)	0.284 6(3)	0.865 2(4)
C(3)	1.253 3(4)	0.524 4(2)	0.826 5(4)	C(17)	0.935 3(6)	0.258 1(3)	0.980 9(4)
C(4)	1.281 0(4)	0.507 1(3)	0.971 3(5)	C(18)	0.665 4(5)	0.215 6(3)	0.840 3(5)
C(5)	1.159 5(5)	0.485 5(3)	1.033 4(4)				

* The *y* coordinate of Cl(1) was fixed to define the origin.

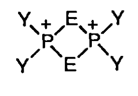
Table 3 Positional parameters and their e.s.d.s for $P(NPr^i_2)_2[NPh(SO_2CF_3)]O$

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
S	0.384 5(1)	0.132 69(8)	0.288 92(6)	C(5)	0.438 2(4)	0.378 6(3)	0.478 1(2)
P	0.558 8(1)	0.274 56(8)	0.222 76(6)	C(6)	0.478 1(4)	0.319 2(3)	0.419 4(2)
F(1)	0.593 6(3)	0.087 5(2)	0.383 8(2)	C(7)	0.524 6(4)	0.236 9(3)	0.064 3(2)
F(2)	0.428 4(3)	0.101 9(2)	0.443 1(1)	C(8)	0.647 1(5)	0.287 7(4)	0.048 6(3)
F(3)	0.449 8(3)	−0.027 5(2)	0.370 8(2)	C(9)	0.536 6(5)	0.121 4(4)	0.066 2(2)
O(1)	0.657 0(2)	0.195 9(2)	0.230 4(2)	C(10)	0.341 5(4)	0.320 8(3)	0.119 6(2)
O(2)	0.256 7(3)	0.135 9(3)	0.305 6(2)	C(11)	0.330 9(5)	0.407 4(4)	0.059 4(3)
O(3)	0.419 3(3)	0.075 3(2)	0.225 0(2)	C(12)	0.241 5(4)	0.238 5(4)	0.093 3(3)
N(1)	0.442 7(3)	0.246 4(2)	0.286 2(2)	C(13)	0.544 9(4)	0.481 3(3)	0.234 6(2)
N(2)	0.471 8(3)	0.278 2(3)	0.135 3(2)	C(14)	0.598 3(5)	0.543 2(3)	0.170 2(3)
N(3)	0.615 8(3)	0.385 1(2)	0.253 1(2)	C(15)	0.539 5(5)	0.547 1(3)	0.307 9(2)
C(1)	0.403 1(4)	0.313 4(3)	0.346 2(2)	C(16)	0.752 9(4)	0.398 0(3)	0.288 2(2)
C(2)	0.289 5(4)	0.365 1(3)	0.332 0(2)	C(17)	0.782 4(4)	0.346 7(4)	0.368 7(3)
C(3)	0.251 1(4)	0.424 8(4)	0.391 3(3)	C(18)	0.847 2(4)	0.365 8(4)	0.233 3(3)
C(4)	0.326 6(5)	0.431 4(3)	0.464 2(2)	C(19)	0.471 5(5)	0.071 3(3)	0.377 5(3)

Table 4 Selected bond lengths (Å) and angles (°)

$PCl(NPr^i_2)_2NPh\cdot AlCl_3$		$P(NPr^i_2)_2[NPh(SO_2CF_3)]O$		$PCl(NPr^i_2)_2NPh\cdot AlCl_3$		$P(NPr^i_2)_2[NPh(SO_2CF_3)]O$	
P(1)–N(1)	1.618(3)		1.785(3)	N(1)–P(1)–Cl(1)	104.0(1)	N(1)–P(1)–O(1)	109.7(2)
P(1)–Cl(1)	2.033(2)	P–O(1)	1.464(3)	N(1)–P(1)–N(2)	112.3(1)		102.1(1)
P(1)–N(2)	1.624(2)		1.649(3)	N(1)–P(1)–N(3)	115.7(1)		104.5(2)
P(1)–N(3)	1.622(3)		1.639(3)	Cl(1)–P(1)–N(2)	106.69(9)	O(1)–P(1)–N(2)	113.9(2)
N(2)–C(7)	1.508(4)		1.504(6)	Cl(1)–P(1)–N(3)	105.0(2)	O(1)–P(1)–N(3)	112.2(2)
N(2)–C(10)	1.511(5)		1.481(6)	N(2)–P(1)–N(3)	112.1(1)		113.5(2)
N(3)–C(13)	1.511(4)		1.490(5)	P(1)–N(2)–C(7)	121.6(2)		119.9(2)
N(3)–C(16)	1.511(5)		1.505(5)	P(1)–N(2)–C(10)	115.8(2)		124.7(2)
C(7)–C(8)	1.514(5)		1.517(7)	C(7)–N(2)–C(10)	122.6(2)		115.5(3)
C(7)–C(9)	1.519(5)		1.533(6)	P(1)–N(3)–C(13)	120.0(3)		122.8(2)
C(10)–C(11)	1.530(5)		1.535(6)	P(1)–N(3)–C(16)	118.4(2)		121.5(3)
C(10)–C(12)	1.530(6)		1.543(6)	C(13)–N(3)–C(16)	121.6(3)		114.8(3)
C(13)–C(14)	1.527(5)		1.538(6)	P(1)–N(1)–C(1)	119.6(2)		126.0(2)
C(13)–C(15)	1.517(5)		1.533(6)	P(1)–N(1)–Al	127.5(1)		120.3(2)
C(16)–C(17)	1.514(5)		1.528(7)	Cl(2)–Al–N(1)	108.21(9)	O(2)–S–N(1)	110.6(2)
C(16)–C(18)	1.535(6)		1.519(6)	Cl(3)–Al–N(1)	111.78(9)	O(3)–S–N(1)	109.5(2)
N(1)–C(1)	1.455(3)		1.458(5)	Cl(4)–Al–N(1)	108.26(9)	C(19)–S–N(1)	106.2(2)
N(1)–Al	1.884(3)	N(1)–S	1.628(3)	Cl(2)–Al–Cl(3)	106.90(6)	O(2)–S–O(3)	121.6(2)
Cl(2)–Al	2.126(1)	S–O(2)	1.422(3)	Cl(2)–Al–Cl(4)	110.49(6)	O(2)–S–C(19)	103.4(2)
Cl(3)–Al	2.127(1)	S–O(3)	1.418(3)	Cl(3)–Al–Cl(4)	111.18(6)	O(3)–S–C(19)	104.1(2)
Cl(4)–Al	2.124(1)	S–C(19)	1.851(4)				

derivative. Therefore, we believe that isolation of the first stable three-co-ordinate methylenephosphonium centre, **2b**, is made possible by steric protection ('kinetic stabilisation') of the P=C bond, which is enhanced by the unusually large twist angle of 60°.[1] The steric shield offered by the phenyl substituent on the nitrogen centre in **2a** is not as uniform or as extensive as two $SiMe_3$ units, and evidently allows interaction between the cation and the anion for oxygen transfer. Thermodynamic control of the products from the imino-system is demonstrated by the fact that $P(NPr^i_2)_2[NPh(SO_2CF_3)]O$ was obtained from $P(NPr^i_2)_2^+$ $SO_3CF_3^-$, by means of a Staudinger reaction (the triflate anion is present prior to formation of the phosphonium



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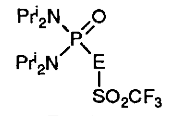

5a E = NPh
5b E = C(SiMe$_3$)$_2$

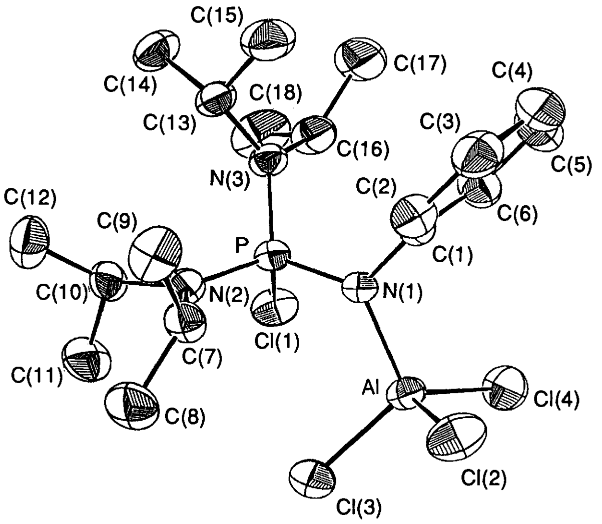

Fig. 1 Crystallographic view of PCl(NPr$^i_2$)$_2$NPh·AlCl$_3$

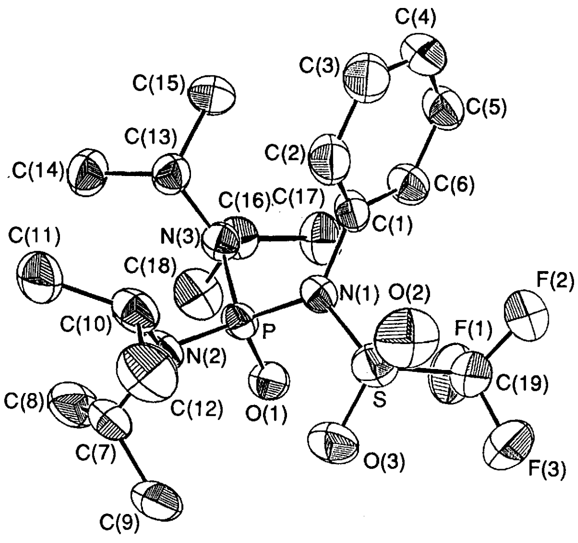

Fig. 2 Crystallographic view of P(NPr$^i_2$)$_2$[NPh(SO$_2$CF$_3$)]O

cation), and from the iminophosphoryl centre [triflate anion is released during reaction with Ag(SO$_3$CF$_3$)].

Alternative Ionic Structures from the Phosphoryl Units.—Retention of a covalent phosphoryl environment for PCl(NR$_2$)$_2$NPh·AlCl$_3$ is consistent with the derivative PCl(NPr$^i_2$)$_2$S·AlCl$_3$.[4] However, other (when R = Me or Et) thio- and seleno-phosphoryl chloride analogues adopt novel dimeric diphosphonium heterocyclic structures **4** in the solid state.[4] Clearly, this delicate thermodynamic ionic/covalent balance is again critically influenced by the degree of steric shielding at the diaminophosphoryl centre. Furthermore, it is interesting that the bis(dimethylamino)(methylimino)- and bis(diethylamino)(ethylimino)-phosphinic halides PX(NR$_2$)$_2$NR (R = Me or Et; X = Cl or Br) undergo an autoionisation to the analogous diphosphonium heterocyclic phosphetidines,[3] while a covalent monomeric phosphoryl structure is observed for the more sterically protected PCl(NPr$^i_2$)$_2$NPh.[22]

Conclusion

The three-co-ordinate diaminoiminophosphonium cation is thermodynamically unstable: the tetrachloroaluminate salt prefers the thermally stable diaminoiminophosphinic chloride–trichloroaluminium Lewis complex covalent alternative, and the triflate salt adopts the triaminophosphine oxide covalent alternative, despite the presence of diisopropylamino-substituents. Therefore, steric shielding at carbon is believed to be responsible for the observed stability of the analogous diaminomethylenephosphonium cation.[1]

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