# Coordination of neutral ligands to a neutral phosphorus system

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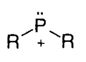
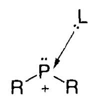
**Structural characterization of complexes involving neutral ligands (quinuclidine and tetramethylethylenediamine) coordinated to a neutral phosphorus system shows unusually long ( > 2.00 Å) N → P coordinative bonds; the bidentate ligand links two phosphorus acceptors.**

Conventional coordination chemistry[1] classifies compounds containing low oxidation state electron-rich elements of groups 15, 16 and 17 as donors (ligands). Nevertheless, compounds such as $I_3^-$, $SF_5^-$ and $PBr_4^{-2}$ represent σ-complexes of halide ions coordinated to 'lone-pair bearing' non-metal acids ($I_2$, $SF_4$, $PBr_3$). Examples of coordination to electron-rich p-block elements by neutral ligands are less obvious, but include cations such as $[I(py)_2]^+$[3] and arene charge-transfer complexes of the halogens[4] and $NO^+$.[5] The acceptor potential for trihalides of phosphorus, arsenic, antimony and bismuth have been demonstrated by vapour-pressure measurements,[6] and phosphenium cations[7] **1** are established as effective acceptors (*e.g.* **2**[8,9] and **3**[10,11]). Such developments highlight a potentially extensive and diverse new area of coordination chemistry. We now report the identification of adducts involving the neutral (zwitterionic) aluminatoiminophosphine **4**[12] (exploiting the analogy[7] with phosphenium cations) with neutral amine and ether bases (ligands).



**1**



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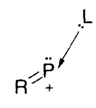

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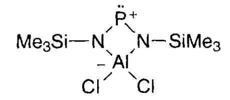

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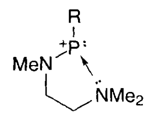

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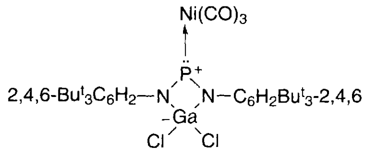

**6**

Reactions† of **4** with quinuclidine (qncd) (1 : 1) and *N,N,N′,N′*-tetramethylethylenediamine (tmen) (2 : 1) are essentially instantaneous at room temperature and each reaction gives a single adduct product ($^{31}P$ NMR), which has been isolated and comprehensively characterized.‡ X-Ray crystal structures (**4**·qncd, Fig. 1 and **4**$_2$·tmen, Fig. 2) reveal that all amine nitrogen centres are bound to phosphorus (two acids bound to one base for **4**$_2$·tmen), and the structural features are comparable to complexes involving these amines with more familiar group 13 acids, $Me_3E$ (E = Al,[13,14] Ga,[2,14] In[15]) and $H_3E$ (E = Al,[16] Ga[17]). The N–P linkages to the ligand [**4**·qncd 2.2038(9) Å; **4**$_2$·tmen 2.110(6) Å] are substantially longer than the 'single' bond in $[O_3PNH_3]^-$ (1.77 Å),[18] the intermolecular coordinative bond in derivatives of **2** [1.796(3) Å][8] and the intramolecular coordinative bonds in **5** [1.84 Å, Y = Cl, anion = $Cl^-$, and 1.88 Å, Y = Ph, anion = $BPh_4^-$][19] and related compounds.[20] To our knowledge, they represent the longest N–P bonds yet reported.

The solid-state $^{31}P$ NMR spectrum of **4**·qncd gives an isotropic chemical shift which is consistent with the solution

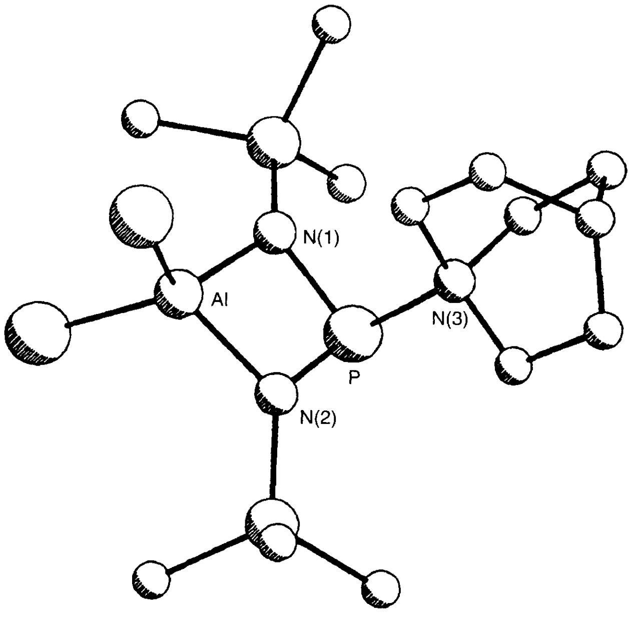

**Fig. 1** Crystallographic view of **4**·qncd. Selected bond lengths (Å) and angles (°): P–N(1), 1.686(9), P–N(2) 1.660(9), P–N(3) 2.038(9), N(1)–Al 1.85(1), N(2)–Al 1.860(9), N(1)–P–N(2) 93.9(5).

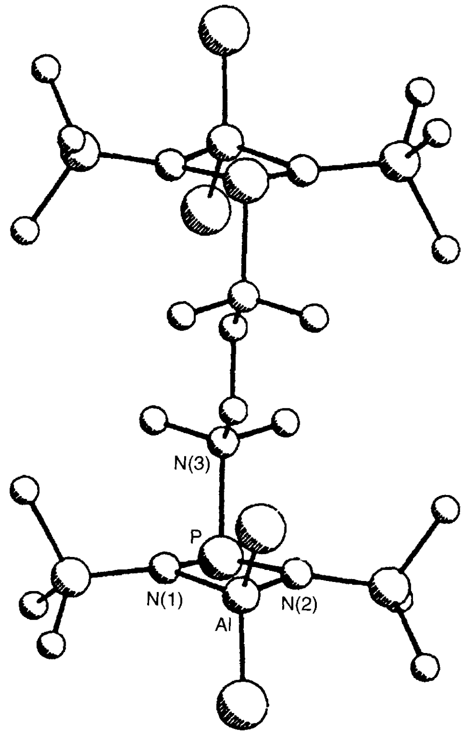

**Fig. 2** Crystallographic view of **4**$_2$·tmen. Selected bond lengths (Å) and angles (°): P–N(1) 1.658(5), P–N(2), 1.661(5), P–N(3) 2.110(6), N(1)–Al 1.863(6), N(2)–Al 1.866(5), N(1)–P–N(2), 94.3(3).

shift (δ 203). However, broad downfield shifted signals are observed for $\mathbf{4}_2$·tmen in solution (δ *ca.* 40–50 relative to isotropic solid-state shift) implying dissociation of one of the ligands and reflecting the reduction in basicity of the uncoordinated nitrogen centre of a diamine after coordination of one of the nitrogen centres. $^{31}$P solution NMR studies of the amine complexes show the appearance of new signals at the expense of the complexes within days indicating a kinetic stability for the isolated complexes.

Similar complexes formed from reactions of **4** with tetrahydrofuran and 1,4-dioxane ($^{31}$P NMR: δ 180 and 184, respectively)§ show solid-state $^{31}$P NMR chemical shift spans ($\Omega$ = 340.7 and 358.1 ppm, respectively) consistent with those observed for the amine complexes (**4**·qncd, $\Omega$ = 382.9; $\mathbf{4}_2$·tmen, $\Omega$ = 454.4 ppm).

In conclusion, the zwitterionic iminophosphine **4** can be considered 'Lewis amphoteric' in view of the recent reports of **6** (involving a gallium derivative of **4**).[21] Tetramethylethylenediamine provides a means of linking phosphorus acceptors and the possibility of macromolecular assembly.

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## Footnotes

† In a typical experiment, solutions of amine and **4** were combined in toluene (50 ml) in an evacuated vessel.[22] The mixture was stirred for 15 min then filtered and slow removal of the solvent *in vacuo* produced colourless crystals. NMR and IR data were recorded as previously described.[11]

‡ **4**·qncd: Quinuclidine (0.33 g, 3.0 mmol), **4** (0.91 g, 3.0 mmol), recrystallized from toluene–*n*-hexane (1 : 1) at −30 °C, yield 0.58 g, 47%; mp 90.5–92.5 °C, satisfactory elemental analysis. IR (cm$^{-1}$): 1484m, 1403w, 1350m, 1318m, 1250s, 1207m, 1088s, 1045m(sh), 988s(br), 907m, 845s(br), 762s, 738s, 687s, 640s, 625m, 580s, 503s, 446w, 359w, 346m, 337w, 309w, 277w, 259w. $^{31}$P NMR (toluene) δ 208, ($CD_2Cl_2$) δ 205; CP-MAS isotropic δ 203, $\delta_{11}$ 446.5, $\delta_{22}$ 98.4, $\delta_{33}$ 63.6, $\Omega$ = 382.9; $^1$H NMR ($CD_2Cl_2$) δ 0.18 (s, 18 H), 1.81 (m, 6 H), 2.03 (m, 1 H), 2.90 (t, 6 H); $^{13}$C NMR ($CD_2Cl_2$) δ 2.9 (s), 21.5 (s), 25.1 (s), 45.7 (s).

*Crystal data*: monoclinic, space group $P2_1/n$, $a$ = 6.900(9), $b$ = 19.442(8), $c$ = 17.25(9) Å, $U$ = 2298(4) Å$^3$, $\beta$ = 96.85(8)°, $Z$ = 4, $D_c$ = 1.198 Mg m$^{-3}$, $\mu$ = 4.91 cm$^{-1}$, $R_w$ = 0.0611.

$\mathbf{4}_2$·tmen: tmen (0.33 g, 2.8 mmol), **4** (1.71 g, 5.64 mmol), yield 0.99 g, 49%; mp 91.0–93.5 °C; satisfactory elemental analysis. IR (cm$^{-1}$): 1476s(sh), 1404s, 1351w, 1336w, 1324w, 1267s(sh), 1249s, 1199w, 1174w, 1113m(sh), 1095s, 1014s(sh), 1003s(br), 943m, 864s(sh), 848s(br), 787s, 756s, 742s, 689s, 641s, 623m, 579s, 506s(br), 458m(sh), 410m, 390w(sh), 354m, 313m, 268w. $^{31}$P NMR (toluene) δ 293, ($CD_2Cl_2$) δ 285; CP-MAS isotropic δ 234, $\delta_{11}$ 523.0, $\delta_{22}$ 109.4, $\delta_{33}$ 68.6, $\Omega$ = 454.4; $^1$H NMR ($CD_2Cl_2$): δ 0.24 (s, 36 H), 2.44 (s, 12 H), 2.76 (s, 4 H); $^{13}$C NMR ($CD_2Cl_2$) δ 2.2, 44.2.

*Crystal data*: triclinic, space group $P\bar{1}$, $a$ = 10.622(3), $b$ = 11.580(4), $c$ = 9.194(5) Å, $U$ = 977.1(7) Å$^3$, $\alpha$ = 105.22(4), $\beta$ = 95.90(4), $\gamma$ = 63.56(2)°, $Z$ = 1, $D_c$ = 1.228 Mg m$^{-3}$, $\mu$ = 5.69 cm$^{-1}$, $R_w$ = 0.0471.

§ Slow removal of solvent left a white solid (0.93 g) which was washed with cold hexanes. **4**·thf: $^{31}$P NMR ($CD_2Cl_2$) δ 180; CP-MAS isotropic δ 195, 192, $\delta_{11}$ 391.7, $\delta_{22}$ 133.8, $\delta_{33}$ 51.0, $\Omega$ = 340.7 ppm, impurity at δ 69. **4**·dioxane: $^{31}$P NMR ($CD_2Cl_2$) δ 184; CP-MAS isotropic δ 169, 167, 165, $\delta_{11}$ 353.6, $\delta_{22}$ 156.8, $\delta_{33}$ −4.5, $\Omega$ = 358.1 ppm, 382 ppm (**4**).

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