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# A simple route to multifunctional phosphide and amide donor sets; syntheses and structures of $[\{Bu^tPAs(NMe_2)_2\}K{\cdot}pmdeta]_2$ and $[\{CyNAs(NMe_2)_2K\}_2]_\infty$

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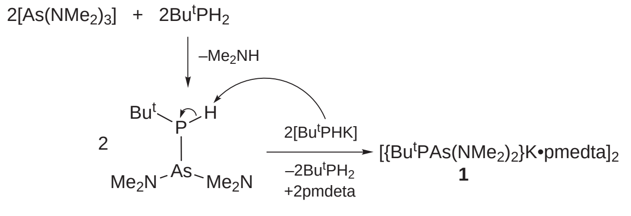
**The syntheses of $[Bu^tPAs(NMe_2)_2K{\cdot}pmedta]_2$ 1 and $[\{CyNAs(NMe_2)_2K\}_2]_\infty$ 2 from the reactions of $[As(NMe_2)_3]$ with $Bu^tPH_2$ and $CyNH_2$, respectively, in the presence of potassiated bases exemplify a general approach to multifunctional secondary phosphide and amide anions containing variable sets of group 15 donor centres.**

Studies of alkali metal phosphoramide (containing $[R_2PNR]^-$)[1] and related hydrazide (containing $[R_2NNR]^-$)[2] complexes have revealed a diverse range of structural types in the solid state for this important class of ligands, in which both the anionic and neutral N and P centres can coordinate the cations. However, to our knowledge the only analogous ligands containing other combinations of group 15 elements to be structurally characterised are $[Bu^t(H)PPBu^t]^-$[3] and $[Bu^t{}_2AsAsBu^t]^-$.[4] We have recently synthesised new polydentate imido and phosphinidene anion ligand systems containing other group 15 elements, such as $[Sb(ER)_3]^{3-}$ (E = N, P),[5] and now report that a related methodology involving dimethylamido group 15 reagents gives the anions $[REAs(NMe_2)_2]^-$. These secondary phosphide and amide anions (related to simple phosphoramides and hydrazides) are a new class of highly functionalised donor ligands.

The reaction of $[As(NMe_2)_3]$ (1 equiv.) with $Bu^tPH_2$/$[Bu^tPHK]$ (1:1 equiv.) can be controlled, giving the stable complex $[\{Bu^tPAs(NMe_2)_2\}K{\cdot}pmdeta]_2$ **1** in the presence of pmdeta [ = $(Me_2NCH_2CH_2)_2NMe$].† This outcome contrasts with the prolonged reactions between $[As(NMe_2)_3]$ and $[Bu^tPHLi]$ (1:3 equiv.) or $[Bu^tPHLi]/Bu^tPH_2$ (1:1:1 equiv.), which yield species containing the cyclic $[(Bu^tP)_3As)]^-$ anion.[6] The reaction producing **1** appears to involve an acid-catalysed process (Scheme 1), as is suggested by the isolation of the related amide complex $[\{CyNAs(NMe_2)_2K\}_2]_\infty$ **2** from the reaction of $[As(NMe_2)_3]$ with $CyNH_2$ in the presence of $[Pr^i{}_2NK]$ (1:1:1 equiv.) as the base.†

The X-ray structures of **1** (Fig. 1) and **2** (Fig. 2)‡ reveal that both species are composed of similar centrosymmetric $K_2P_2$ and $K_2N_2$ dimeric units in the solid state, in which two $K^+$ cations are bridged by the anionic P and N centres of their respective $[Bu^tPAs(NMe_2)_2]^-$ and $[CyNAs(NMe_2)_2]^-$ ligands. The K–P bond lengths in **1** [K(1)–P(1) 3.315(4), K(1)–P(1a) 3.462(3)Å] and K–N distances in **2** [K(1)–N(1) 2.893(6) to K(1)–N(1A) 2.780(7) Å] within these dimer units are similar to those found in the few structurally characterised K phosphide[3,7] and amide[8] complexes. The $K^+$ cation in each complex further interacts with one of the $Me_2N$ groups [K(1)–N(5) 2.991(8) in **1**, K(1)–N(3) 2.852(7)Å in **2**] to form a four-membered chelate ring. Further aggregation of the dimeric units of **1** is prevented by coordination of the $K^+$ cations by pmdeta, resulting in a distorted octahedral geometry at the metal centres. However, the absence of Lewis base solvation in **2** leads to the association of the dimers, *via* the second $Me_2N$ group of each $[CyNAs(NMe_2)_2]^-$ anion [K(1)–N(2B) 3.071(7) Å], giving a novel poymeric chain structure. This arrangement results in a distorted-tetrahedral geometry for the $K^+$ centres and in the formation of puckered centrosymmetric $[KNAsN]_2$ rings which link the $K_2N_2$ dimer units of **2** together. The low coordination number of the $K^+$ cations of **2** appears to be compensated for by extensive, relatively short[9] Cy $\alpha$-C···K and Me C···K contacts [K(1)···C 3.26–3.48Å].

Comparison with other As–P[10] and As–N[11] bonded compounds reveals that the As–P and As–N bonds in **1** [As(1)–P(1) 2.260(3) Å] and **2** [As(1)–N(1) 1.782(7) Å] are at the lower end of the range of values observed for single bonds, and in **2** this bond is significantly shorter than the two $As–NMe_2$ bonds (mean 1.914 Å). It seems most likely that the relatively short As–P bond in **1** largely stems from the effect of polarisation, with the geometry about the anionic P centre in this complex giving no indication of any partial multiple bonding [*e.g.* C(14)–P(1)–As(1) 98.1(3)°]. However, the bond angle at the



**Scheme 1**

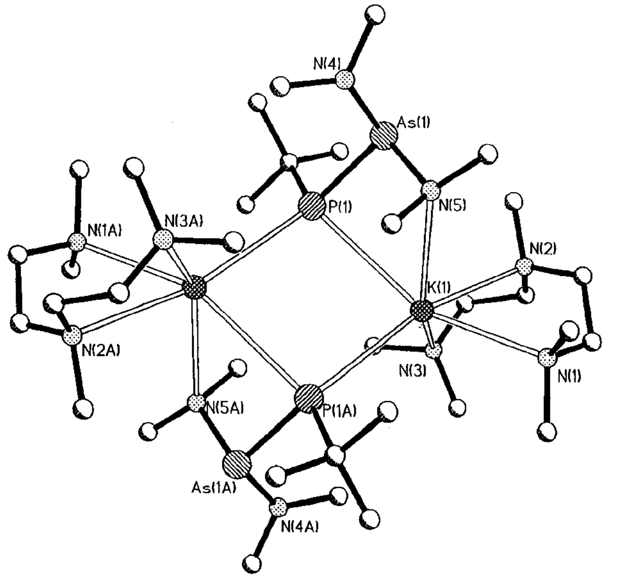


**Fig. 1** Dimer structure of **1**. H atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): P(1)–K(1) 3.315(4), P(1A)–K(1) 3.462(3), N(5)–K(1) 2.991(8), mean N(1,2,3)–K 2.93, As(1)–P(1) 2.260(3), N(4)–As(1) 1.869(9), As(1)–N(5) 1.877(9), K(1)–P(1)–K(1A) 96.98(8), P(1)–K(1)–P(1A) 93.02(8), C(14)–P(1)–As(1) 98.1(3), P(1)–As(1)–N(4) 107.1(3), P(1)–As(1)–N(5) 97.7(2), N(4)–As(1)–N(5) 100.7(4), As(1)–N(5)–K(1) 101.9(3).

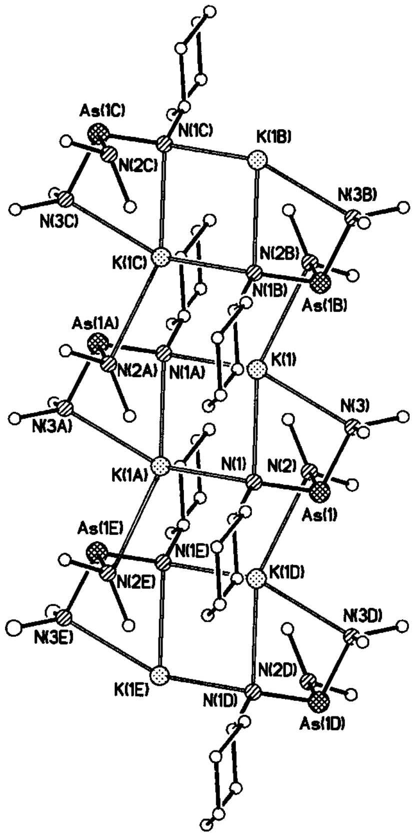


**Fig. 2** Part of the infinite polymeric structure of **2** which runs along the *a*-axis of the unit cell. H atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): K(1)–N(1) 2.893(6), K(1)–N(1A) 2.780(7), K(1)–N(3) 2.852(7), K(1)–N(2B) 3.071(7), Cy $\alpha$-C(–H) and Me C(–H) K(1)···C 3.26-3.48, As(1)–N(1) 1.782(7), As(1)–N(2) 1.894(7), As(1)–N(3) 1.935(6), K(1)–N(1)–K(1A) 87.9(2), N(1)–K(1)–N(1A) 92.1(2), C(1)–N(1)–As(1) 117.4(6), N(1)–As(1)–N(2) 98.9(3), N(1)–As(1)–N(3) 99.8(3), N(2)–As(1)–N(3), 97.5(3), As(1)–N(3)–K(1) 97.3(3).

anionic N centre in **2** [C(1)–N(1)–As(1) 117.4(6)°] may indicate that there is some contribution from $p_\pi$–$d_\pi$ interaction, an effect which may be exacerbated by the elongation of the As–N bond involved in the chelate ring [As(1)–N(3) 1.935(6); *cf.* As(1)–N(2) 1.894(7)].

In conclusion, the synthetic route used in the preparation of **1** and **2** is potentially applicable to an extensive series of related group 15 anions. The $[Bu^tPAs(NMe_2)_2]^-$ and $[CyNAs(NMe_2)_2]^-$ anions **1** and **2** represent a unique set of readily accessible new ligands, containing combinations of group 15 elements within their frameworks (all of which being capable potentially of coordinating a metal centre). The structural studies of **1** and **2** provide the first indication of the coordination chemistry and structural trends in these species. The structure of **2** is particularly noteworthy, being composed of a polymer of dimers rather than having a more conventional ladder arrangment.[12]

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## Notes and references

† *Syntheses* **1**: $[Bu^tPHK]$ was prepared by the reaction of $PhCH_2K$ (0.78 g, 6.0 mmol) with $Bu^tPH_2$ (0.4 ml, 6.0 mmol) in hexane (10 ml)/thf (5 ml) under argon. After stirring the reaction at room temp. (30 min.) it was cooled (−78 °C) and a mixture of $[As(NMe_2)_3]$ (6.0 mmol, 2.4 ml, 2.5 mol dm$^{-3}$ in hexane) and $Bu^tPH_2$ (0.4 ml, 6.0 mmol) in hexane (10 ml) [which had previously been stirred at room temp. (30 min.)] was added. Excess pmdeta (7.1 mmol, 1.5 ml) was added and the reaction was allowed to warm to room temperature. Removal of the solvent under vacuum and addition of hexane (17 ml) gave a precipitate. Addition of thf (5 ml) and gentle heating dissolved the solid. Storage at −30 °C gave colourless crystals of **1**. First batch yield 0.30g (11%). mp 121 °C (decomp. to a brown solid). $^{31}P$ NMR (MHz, +25 °C, $d_8$-thf, rel. to 80% $H_3PO_4$–$D_2O$), $\delta$−5.91(s). Satisfactory elemental analyses (C,H,N,P) were obtained for **1**.

**2**: $[Pr^i_2NK]$ (6.0 mmol) was prepared by the reaction of $PhCH_2K$ (0.78 g, 6.0 mmol) with $Pr^i_2NH$ (0.85 ml, 6 mmol) in hexane (20 ml)–toluene (10 ml). After heating to reflux and stirring at room temp. (30 min.), a mixture of $[As(NMe_2)_3]$ (3.9 ml, 1.55 mmol dm$^{-3}$ in hexane, 6.0 mmol) and $CyNH_2$ (0.69 ml, 6.0 mmol) in hexane (10 ml) [which had previously been heated to reflux and stirred at room temperature (30 min.)] was added. After stirring at room temperature (10 min.) a green solution was formed with a small amount of precipitate. Gentle heating dissolved the solid and storage at −30 °C (24 h) gave yellow crystals of **2**. First batch yield 0.14 g (8%). $^1H$ NMR (250 MHz, +25 °C, $d_8$-thf), $\delta$ 2.60 (s., 12H, $Me_2N$), *ca.* 3.3–1.0 (collection of overlapping mult., 11 H, Cy). Satisfactory elemental analyses (C,H,N) were obtained for **2**.

‡ *Crystal data*: **1**: $C_{34}H_{84}As_2K_2N_{10}P_2$, $M$ = 923.09, monoclinic, space group $P2_1/n$, $Z$ = 2, $a$ = 14.014(3), $b$ = 12.750(4), $c$ = 15.014(3) Å, $\beta$ = 105.48(3)°, $U$ = 2585.4(10) Å$^3$, $\mu$(Mo-K$\alpha$) = 1.547 mm$^{-1}$, $T$ = 180(2) K. Of a total of 3473 data collected 3357 were independent ($R_{int}$ = 0.098). An empirical absorption correction based on $\psi$-scans was used. The structure was solved by direct methods and refined by full-matrix least squares on $F^2$ to final values of $R1[F > 4\sigma(F)]$ = 0.075 and $wR2$ = 0.189 (all data).[13]

**2**: $C_{10}H_{23}AsKN_3$, $M$ = 299.33, triclinic, space group $P\overline{1}$ (no. 2), $Z$ = 2, $a$ = 6.3524(13), $b$ = 10.275(2), $c$ = 10.957(2) Å, $\alpha$ = 91.31(3), $\beta$ = 99.86(3), $\gamma$ = 95.73(3)°, $U$ = 693.5(2) Å$^3$, μ(Mo-K$\alpha$) = 2.728 mm$^{-1}$, $T$ = 223(2) K. Of a total of 2427 data collected, 1880 were independent ($R_{int}$ = 0.283). The structure was solved by the Patterson method and refined by full-matrix least squares on $F^2$ [13,14] to final values of $R1$ $[I > 2\sigma(I)]$ = 0.0620, $wR2$ = 0.1970 (all data).

CCDC 182/1193. See http://www.rsc.org/suppdata/cc/1999/739/ for crystallographic files in .cif format.

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