

Synthesis and structure of $[(\text{Bu}^t\text{P})_2\text{H}]\text{K}\cdot\text{pmdeta}]_2$, containing an organo diphosphido ligand $[\text{pmdeta} = (\text{Me}_2\text{NCH}_2\text{CH}_2)_2\text{NMe}]$

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Reduction of $[\text{Bu}^t\text{P}]_4$ with K metal (1 : 5 equiv.) followed by the addition of pmdeta and stoichiometric hydrolysis gives $[(\text{Bu}^t\text{P})_2\text{H}]\text{K}\cdot\text{pmdeta}]_2$, a unique complex containing a $[\text{Bu}^t\text{P}(\text{H})\text{PBu}^t]^-$ anion ligand homologous with a phosphido anion (R_2P^-).

Early investigations showed that the reduction of $[\text{RP}]_4$ by alkali metals leads to fragmentation of the cyclic P_4 rings, giving species containing various anions {such as $[\text{RP}]_4^{2-}$, $[\text{RP}]_3^{2-}$, $[\text{RP}]_2^{2-}$ and $[(\text{RP})_2(\text{H})]^-$ } depending on the reaction stoichiometries.¹ However, the solids isolated were mainly characterised by elemental analysis and NMR spectroscopic studies on these and related systems indicated later that mixtures of anions are produced in solution.² Owing to the lack of X-ray structural data on the alkali metal complexes and the difficulty in isolating the pure components there have been few systematic investigations of the coordination chemistry of the organopolyposphido anions and their reactivity with other metal centres is poorly understood.³ Our emerging interest in the potential use of these anions as ligands to main group elements has led us to reinvestigate the reduction of $[\text{Bu}^t\text{P}]_4$ with alkali metals, with the aim of developing well defined reagents for transmetallation.

We report here that the reaction of $[\text{Bu}^t\text{P}]_4$ with potassium metal (1 : 5 equiv.) in thf followed by the addition of pmdeta and stoichiometric hydrolysis gives the crystalline complex $[(\text{Bu}^t\text{P})_2\text{H}]\text{K}\cdot\text{pmdeta}]_2$ **1** (Scheme 1).[‡] This complex is the first representative of this type of alkali metal complex to be fully characterised in pure form. Evidence for the presence of the H atom in the anion of **1** is obtained from the IR spectrum ($\nu_{\text{P-H}}$ 2005 cm^{-1}). In addition, the room-temperature ^{31}P NMR spectrum is similar to that previously reported for $[(\text{Bu}^t\text{P})_2\text{H}]\text{K}$ in thf (produced in trace amounts in the reaction of K metal with $[\text{Bu}^t\text{P}]_4$),^{2a} although with a markedly larger $^1J_{\text{PH}}$ coupling constant in **1** (ca. 201 Hz;⁵ cf. ca. 137 Hz^{2a}). The ^{31}P NMR spectrum illustrates that the anion has a rigid structure in solution in which the proton is bonded solely to one P centre (with no intra- or inter-molecular exchange occurring).

The low-temperature X-ray structure of **1** shows that it exists as dimeric molecules in the solid state in which two $[(\text{Bu}^t\text{P})_2\text{H}]^-$ anions are associated into a ring structure by two pmdeta-solvated K^+ cations [Fig. 1(a)]. Although a number of lithium organophosphides (containing R_2P^-) have been structurally characterised in recent years,⁶ very few complexes of the heavier alkali metals have been reported.⁷ Complex **1** is the first containing an organodiphosphido anion, the second homologue of a potential series of organo polyphosphido chain anions of the

type $[\text{R}_{2x+1}\text{P}_x]^-$. The closest analogues of **1** are phosphoramides⁸ such as the dimer $[(\text{Ph}_2\text{PN}(\text{Ph}))\text{Li}\cdot\text{Et}_2\text{O}]_2$, containing a $[(\text{Ph}_2\text{PN}(\text{Ph}))]^-$ anion.^{8a} The only other alkali metal organo polyphosphido to be reported is $[(\text{Bu}^t\text{P})_2\text{P}]\text{Li}\cdot 2\text{thf}$, containing a 'branched' $[(\text{Bu}^t\text{P})_2\text{P}]^-$ anion.⁹

The anionic P centres of the $[(\text{Bu}^t\text{P})_2\text{H}]^-$ ligands form the central K_2P_2 ring of the dimeric structure of **1** [K(1)–P(1) 3.340(3), K(1)–P(1a) 3.251(2) Å]. Secondary coordinative interactions occur with the neutral P centres of each $[(\text{Bu}^t\text{P})_2\text{H}]^-$ anion [P(2)–K(1) 3.658(3) Å]. The bidentate

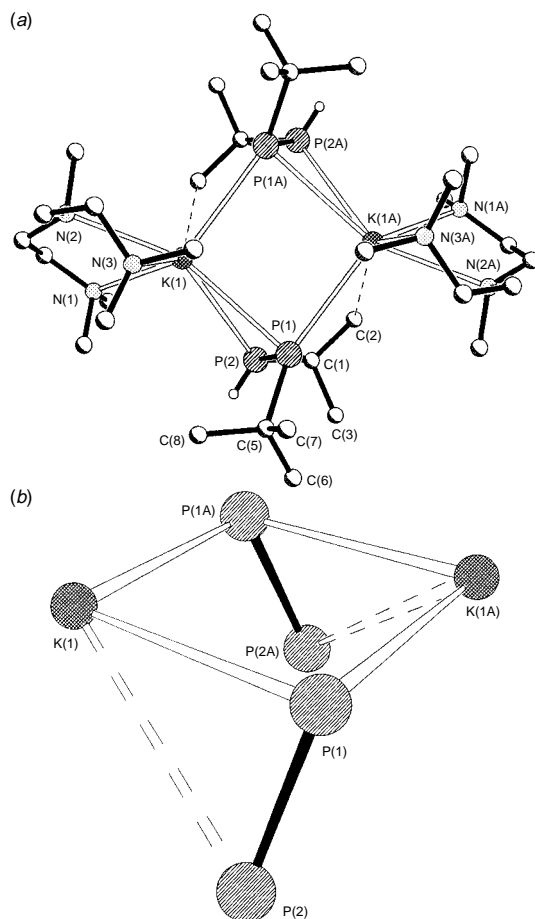
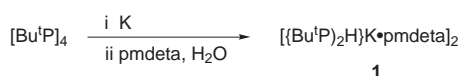


Fig. 1 Dimer structure of **1**. H atoms (except that bonded to P) have been omitted for clarity. Key bond lengths (Å) and angles ($^\circ$): K(1)–P(1a) 3.251(2), K(1)–P(1) 3.340(3), K(1)–P(2) 3.658(3), P(1)–P(2) 2.135(3), K(1)–N(1) 2.936(6), K(1)–N(2) 2.865(6), K(1)–N(3) 2.894(7), K(1a)–C(2) 3.685(3) [K(1)–H(2a) 3.01]; P(1)–K(1)–P(1a) 94.98(6), K(1)–P(1)–K(1a) 84.93(6), P(1)–K(1)–P(2) 35.15(5), P(2)–P(1)–K(1) 84.93(6), P(2)–P(1)–K(1a) 110.11(9).



Scheme 1

coordination mode of the $[(\text{Bu}^t\text{P})_2\text{H}]^-$ ligands in **1** is similar to that found in dimeric alkali metal phosphoramides⁸ and hydrazides,¹⁰ in which P,N and N,N chelation of the alkali metals by the $[\text{R}_2\text{PNR}]^-$ and $[\text{R}_2\text{NNR}]^-$ anions occurs. However, one significant difference with the latter is the unusual *cis* orientation of the $[(\text{Bu}^t\text{P})_2\text{H}]^-$ ligands with respect to the K_2P_2 dimer ring of **1** [giving a 'boat-like' rather than 'chair-like' core, Fig. 1(b)]. This orientation seems most likely to be steric in origin. A noteworthy feature in **1** is the presence of a relatively short P–P bond [2.135(3) Å] which is well below distances normally anticipated for single bonds (*ca.* 2.20 Å) and similar to those found in transition metal complexes containing $\eta^2\text{-RP=PR}$ ligands (*ca.* 2.1 Å).³ In dimeric complexes containing isoelectronic $[\text{R}_2\text{NNR}]^-$ anions the N–N bonds are generally longer than in neutral hydrazines, as a result of enhanced lone pair repulsion.¹⁰ The shortening of the P–N bonds in complexes containing $[\text{R}_2\text{PNR}]^-$ ligands may partly be a result of $p_\pi(\text{N})\text{-d}_\pi(\text{P})$ bonding. However, although the possibility of such bonding cannot be discounted in the $[(\text{Bu}^t\text{P})_2\text{H}]^-$ anion the principal reason for the short P–P bond length probably stems from compression arising from the chelation of the K^+ cations.

The isolation and full characterisation of **1** provides a well defined and readily accessible source of the $[(\text{Bu}^t\text{P})_2\text{H}]^-$ anion for application as a ligand to a range of metals. In addition, the presence of a reactive proton also furnishes the potential for further metallation. In this regard preliminary ³¹P studies indicate that the major product formed by the reaction of **1** with Bu^tLi is not the expected $[(\text{Bu}^t\text{P})_2]^{2-}$ dianion but the $[(\text{Bu}^t\text{P})_3]^{2-}$ dianion.†

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Notes and References

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‡ *Synthesis* of **1**: to a solution of $[(\text{Bu}^t\text{P})_4]$ (1.0 g, 2.84 mmol)^{1a} in thf (40 ml) was added K metal (0.56 g, 14.2 mmol) and the mixture brought to reflux for 24 h. After this period all the K had reacted (if 8 equiv. are used then only 5 equiv. is consumed even after reflux for 48 h). The mixture was filtered while hot (Celite) and pmdeta (2.1 ml, 10 mmol, distilled over Na) was added. The orange–yellow solution was cooled (–78 °C) and a standard solution of H_2O in thf was added dropwise (10.2 ml, 0.56 mol dm^{-3} , 5.68 mmol). The mixture was allowed to warm to room temperature and stirred (12 h), resulting in a yellow solution and the precipitation of KOH. Filtration (Celite) followed by concentration to *ca.* 8 ml gave a light yellow precipitate which was heated into solution. Storage at 25 °C (12 h) gave large light yellow crystalline needles of **1**; yield 0.33 g (15%) (the low yield reflects the high solubility of the complex in thf); decomp. > 115 °C to orange oil; IR (Nujol), 2205m (P–H str.), other major bands at 1345m, 1309m, 1162s, 1023s, 945m, 900m, 809m, 784m; ¹H NMR (250 MHz, +25 °C, $[\text{C}_6\text{D}_6]$ thf), δ 2.75 (1 H, br d, P–H, $J_{\text{H}^1\text{P}}$ *ca.* 200 Hz), 2.34 (8 H, m, CH_2CH_2 of pmdeta),

2.21 (3 H, s., NMe of pmdeta), 2.13 (12 H, s., NMe_2 of pmdeta), 1.15 (9 H, br s, Bu^t), 0.99 (9 H, br s, Bu^t); ³¹P NMR (101.256 MHz, +25 °C, $[\text{C}_6\text{D}_6]$ thf, rel. to 85% H_3PO_4), δ –8.90 (dd, Bu^tPH , $J_{\text{H}^1\text{P}}$ 201.4 ± 1.1, $J_{\text{P}^1\text{P}^2}$ 321.5 Hz), –57.37 (d Bu^tP , $J_{\text{P}^1\text{P}^2}$ 321.5 Hz), the ¹H decoupled spectrum gave $J_{\text{P}^1\text{P}^2}$ 321.6 ± 0.6 Hz; Anal., Calc. for $[\text{C}_{17}\text{H}_{42}]_2\text{P}_2\text{N}_3\text{K}_2$: C, 52.4; H, 10.8; N, 10.8; P, 15.9. Found: C, 50.2; H, 10.5; N, 10.5; P 15.3%. The reaction of **1** with Bu^tLi (*ca.* 1 equiv.) in thf was monitored by ³¹P NMR spectroscopy (+25 °C). This preliminary study reveals that the major product contains the $[(\text{Bu}^t\text{P})_3]^{2-}$ dianion, with a triplet (δ 4.74) and a doublet (δ –44.96) being observed (ratio 1 : 2 respectively, $J_{\text{P}^1\text{P}^2}$ *ca.* 170 Hz).

§ *Crystal data* for **1**: $\text{C}_{34}\text{H}_{84}\text{K}_2\text{N}_6\text{P}_4$, $M = 779.15$, orthorhombic, space group $Pnm2$, $a = 14.457(7)$, $b = 16.255(8)$, $c = 10.502(5)$ Å, $U = 2468(2)$ Å³, $Z = 2$, $D_c = 1.048$ g cm^{-3} . Data were collected on a Siemens-Stoe AED diffractometer (2θ – ω scans) using an oil-coated¹¹ rapidly cooled crystal of dimensions 0.30 × 0.30 × 0.25 mm ($3.64 < \theta < 22.48^\circ$). Of a total of 3410 reflections collected, 3052 were independent ($R_{\text{int}} = 0.036$). An absorption correction based on ψ -scans was applied (max./min. transmission = 0.978/0.618). The structure was solved by direct methods and refined by full-matrix least squares on F^2 using all data to final values of $R1$ [$F > 4\sigma(F)$] = 0.058 and $wR2 = 0.140$;¹² largest peak, hole in the final difference map = 0.30, –0.32 e Å^{–3}. All non-hydrogen atoms were refined anisotropically and H-positions were set geometrically. C-atoms of the pmdeta ligand were disordered and were split into two positions using restraints. CCD8 182/900.

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