Synthesis and solid-state structure of [K$_3$(thf)$_2${PH(Mes)}$_3$]$_\infty$ (Mes = 2,4,6-Me$_3$C$_6$H$_2$): the first potassium phosphanide with a polyhedral arrangement of K and P atoms

Christoph Frenzel, Peter Jörchel and Evamarie Hey-Hawkins*†

Institut für Anorganische Chemie der Universität Leipzig, Talstrasse 35, D-04103, Leipzig, Germany

KPH(Mes) (Mes = 2,4,6-Me$_3$C$_6$H$_2$), prepared from potassium and PH$_2$(Mes) in refluxing toluene, crystallises from thf–pentane as [K$_3$(thf)$_2${PH(Mes)}$_3$]$_\infty$ 1, in which the basic structural feature is a chain of tetragonal pyramids of KP$_5$ units, which share common edges, and two additional K atoms located over two adjacent edges of one trigonal face of the pyramid.

While lithium phosphanides have been widely employed as phosphanide-transfer reagents,[1] their heavier congeners have remained largely unexplored. Furthermore, most structural studies have focused on the solid-state structures of lithium phosphanides,[2,3] and little is known about the structures of the heavier alkali metal analogues. A few examples of sodium,[3,4] potassium,[3a,5] and caesium phosphanides[4] have been reported, most of which, like the majority of lithium derivatives, exhibit dimeric M$_2$P$_2$ arrangements or polymeric one-dimensional ladders[5] consisting of alternating M–P and P–M steps. Lithium phosphanides also form one-dimensional polymeric zigzag or helical –M–P–M–P– chains.

In our studies on potential phosphinidene (PR) precursors, we are interested in the synthesis and solid-state structures of P–H functionalised alkali metal phosphanides, MPHR. We now report the synthesis and solid-state structure of [K$_3$(thf)$_2${PH(Mes)}$_3$]$_\infty$ 1.

When KPH(Mes)‡ is extracted with thf and the solution (10 ml) layered with pentane (10 ml), yellow crystals of [K$_3$(thf)$_2${PH(Mes)}$_3$]$_\infty$ 1 are obtained on standing for two weeks at room temperature (yield of isolated product: 80%). 1 is insoluble in toluene or pentane and sparingly soluble in ether, but dissolves rapidly in thf. The proton-coupled ^{31}P NMR spectrum§ in thf exhibits a doublet a δ −141.6, which is shifted to low field relative to PH$_2$(Mes) (δ −153.9)[6] and Li(thf)$_2${PH(Mes)} (δ −163.4).[7]¶ The $^1J_{PH}$ coupling constant of 156 Hz is lower than those of PH$_2$(Mes) (207.3 Hz)[6] and Li(thf)$_2${PH(Mes)} (187 Hz).[7]

1 crystallises in the centrosymmetric monoclinic space group $P2_1/n$.‖ The asymmetric unit contains three types of potassium and phosphorus atoms. Potassium atom K(1) is surrounded in a tetragonal-pyramidal fashion by five P atoms, two of which [P(1A) and P(2A)] are generated by the 2$_1$ axis. Furthermore, the 2$_1$ axis generates a polymeric chain of edge-sharing tetragonal pyramids in which the apical P atoms alternately point upwards and downwards (Fig. 1). Potassium atom K(1) is almost coplanar with P(1), P(2), P(1A), P(2A) (deviation 0.08 Å), and the pyramidal structure is only slightly distorted, the P–K–P angles ranging from 88.28(4) to 92.32(4)°. The K–P distances range from 3.306(2) to 3.451(1) Å and are comparable to those in KPH(Mes*) [Mes* = 2,4,6-Bu$^t_3$C$_6$H$_2$, K–P 3.271(2), 3.181(2), 3.357(2) Å],[5] which, however, has an infinitely extended, centrosymmetric ladder structure, and the related compound [K(thf)$_2${P(Mes)(SiFBu$^t_2$)}]$_2$ [K–P 3.230(1) Å].[3a] Similar K–P distances are also found in [Cp*$_2$ZrP$_3$K(thf)$_{1.5}$] [Cp* = C$_5$Me$_5$, K–P 3.37(1)–3.61(1) Å],[8,9] [Cp$_2$ZrH{P(Mes*)}K(thf)$_2$]$_2$ [K–P 3.497(9), 3.67(1) Å],[9] a potassium phospholide [K–P 3.264(1), 3.256(1) Å],[10] and a

phospholylsamarium complex [(PC$_4$Me$_4$)$_6$Sm$_2$(KCl)$_2$-(C$_6$H$_5$Me)$_3$]$_\infty$ [K–P 3.263(5), 3.383(5) Å].[11] In the solid-state compound KP, a polymeric helical chain of P atoms [$^1_\infty$ (P$^-$)] is surrounded by K atoms with short distances of 3.08–3.39 Å, and longer distances of 3.62–3.86 Å.[12]

The two remaining potassium atoms of 1, K(2) and K(3), are located above the adjacent edges, P(3)–P(2A) and P(3)–P(1A), respectively, of a P$_3$ face of the tetragonal pyramid, with K–P distances in the expected range of 3.29–3.35 Å (Fig. 1). Both K atoms interact weakly with a third P atom [K(2)–P(1) 3.669(1), K(3)–P(2) 3.936(2) Å]. The coordination environment around the K(2) and K(3) atoms (Figs. 2 and 3) is completed by a disordered thf molecule and K–aryl interaction [η^3 and η^1
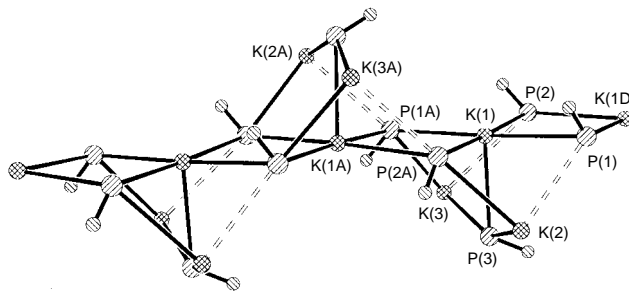

Fig. 1 Arrangement of the KP$_5$ fragment of 1 (SHELXTL PLUS; XP).[15] Only the K, P and H atoms (of P–H) are shown. Selected bond lengths (Å) and angles (°): K(1)–P(1) 3.368(1), K(1)–P(2) 3.397(1), K(1)–P(1A) 3.364(1), K(1)–P(2A) 3.451(1), K(1)–P(3) 3.306(2); P(1)–K(1)–P(2) 90.88(3), P(2)–K(1)–P(1A) 89.25(4), P(1A)–K(1)–P(2A) 91.46(3), P(2A)–K(1)–P(1) 88.28(4), P(1)–K(1)–P(1A) 177.25(3), P(2)–K(1)–P(2A) 177.23(3), P(1)–K(1)–P(3) 91.52(4), P(2)–K(1)–P(3) 90.34(4), P(1A)–K(1)–P(3) 91.23(4), P(2A)–K(1)–P(3) 92.32(4).
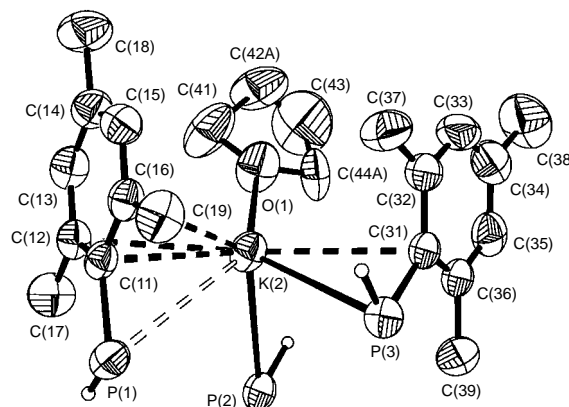

Fig. 2 Environment around K(2) (ORTEP, 50% probability, SHELXTL PLUS; XP).[15] Only one position of the disordered thf and the P–H hydrogen atoms are shown. Selected bond lengths (Å): K(2)–O(1) 2.654(3), K(2)–P(1) 3.669(1), K(2)–P(2A) 3.354(2), K(2)–P(3) 3.323(2), K(2)–C(31) 3.329(4), K(2)–C(12) 3.199(4), K(2)–C(11) 2.991(3), K(2)–C(16) 3.238(4).
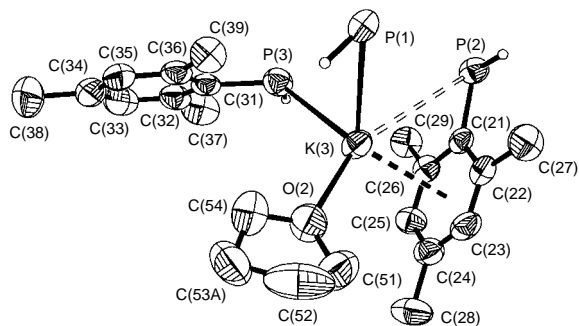
Fig. 3 Environment around K(3) (ORTEP, 50% probability, SHELXTL PLUS; XP).[15] Only one position of the disordered thf and the P–H hydrogen atoms are shown. Selected bond lengths (Å): K(3)–O(2) 2.666(3), K(3)–P(1A) 3.324(2), K(3)–P(2) 3.936(2), K(3)–P(3) 3.291(2), K(3)–C(21) 3.013(3), K(3)–C(22) 3.076(4), K(3)–C(23) 3.226(4), K(3)–C(24) 3.344(4), K(3)–C(25) 3.269(4), K(3)–C(26) 3.125(4).

coordination of the mesityl rings of P(1) and P(3) to K(2), and η^6 coordination of the mesityl ring of P(2) to K(3)] with K–C distances of 2.991(3)–3.344(4) Å. Similarly, K–aryl interaction was observed in KPH(Mes*) [η^3 coordination of Mes*, K–C 2.884(4)–3.197(4)], which is obtained solvent-free even on crystallisation from thf–toluene.[5]

In **1**, which was crystallised from thf–pentane, π interaction with the aryl rings is apparently preferred to coordination of additional thf molecules. Similarly, π coordination of arene ligands to potassium[11,13] and the heavier alkali metals[14] has often been reported in the literature. The caesium phosphanide [Cs(thf)$_{0.5}$P(SiPr$^i_3$){Si(F)(Is)$_2$}]$_\infty$ (Is = 2,4,6-Pr$^i_3$C$_6$H$_2$) also exhibits η^3 and η^6 coordination of the aryl rings of the Is substituents to Cs.[4]

The alkali metal phosphanide presented here is the first example of a potassium phosphanide with a polyhedral arrangement of K and P atoms, in contrast to the corresponding lithium phosphanide, [Li(thf)$_2${PH(Mes)}]$_\infty$,[7] which has a helical one-dimensional Li–P–Li–P arrangement. More information on the structural diversity of alkali metal phosphanides will be needed before the factors that determine the structural arrangement in the solid state are fully understood.

Notes and References

† E-mail: hey@server1.rz.uni-leipzig.de

‡ The preparations were carried out under argon by Schlenk techniques. KPH(Mes) was prepared from K (1.00 g, 25.5 mmol) and excess PH$_2$(Mes)[6] (4.00 ml) in refluxing toluene (50 ml) (2 days), yield: quantitative.

§ In thf, one drop C$_6$D$_6$ for lock, 25 °C, Bruker DRX Avance 400, 161.9 MHz. ^{1}H NMR (400 MHz, [^{2}H$_8$]thf, 25 °C): δ 6.38 (s, 2 H, 2,4,6-Me$_3$C$_6$$H_2$), 2.11 (s, 6 H, o-Me in 2,4,6-Me$_3$C$_6$H$_2$), 2.01 (s, 3 H, p-Me in 2,4,6-Me$_3$C$_6$H$_2$), 1.88 (d, 1 H, P–H, $^1J_{PH}$ 156 Hz). ^{13}C NMR (100.6 MHz, [^{2}H$_8$]thf, 25 °C): δ 20.8 (p-CH$_3$ in 2,4,6-Me$_3$C$_6$H$_2$), 24.9 (o-CH$_3$ in 2,4,6-Me$_3$C$_6$H$_2$), 122.26 (p-C in 2,4,6-Me$_3$C$_6$H$_2$), 127.00 (m-C in 2,4,6-Me$_3$C$_6$H$_2$), 134.22 (o-C in 2,4,6-Me$_3$C$_6$H$_2$), 155.8 (br, $ipso$-C in 2,4,6-Me$_3$C$_6$H$_2$, no P–C coupling observed). IR for **1** (KBr) cm^{-1}: 2316, 2293m (P–H). Mp 189–207 °C.

‖ *Crystal data* for [K$_3$(thf)$_2${PH(Mes)}$_3$]$_\infty$: C$_{35}$H$_{52}$K$_3$P$_3$, *M* = 714.98, yellow crystals, 0.45 × 0.20 × 0.15 mm, monoclinic, space group $P2_1/n$ (no. 14), *T* = 213(2) K, *a* = 16.511(3), *b* = 9.692(2), *c* = 25.337(5) Å, β = 97.72(3), *U* = 4017.9(14) Å^3, *Z* = 4, D_c = 1.182 Mg m^{-3}, *F*(000) = 1520, μ(Mo-Kα) = 0.486 mm^{-1}, 16 463 reflections collected with 1.4 < θ < 26.2°; of these 6909 were independent; 483 parameters, refinements converge to $R1$ = 0.0611, $wR2$ = 0.1175 [for reflections with $I > 2\sigma(I)$], $R1$ = 0.0818, $wR2$ = 0.1275 (all data). Data (Mo-Kα = 0.710 73 Å) were collected with a Siemens CCD (SMART). All observed reflections (2θ range: 2.8–52.4°) were used for determination of the unit cell parameters. The structure was solved by direct methods (SHELXTL PLUS[15]) and subsequent difference Fourier syntheses and refined by full-matrix least squares on F^2 (SHELXTL PLUS[15]); thf treated as disordered groups in two positions [C(42), C(44), A : B = 43 : 57; C(53), A : B = 73 : 27%]. K, P, O and C atoms anisotropic, H atoms of CH$_3$ groups and thf in idealized positions and refined isotropically, H atoms of P–H and C$_6$H$_2$ groups located and refined isotropically. Empirical absorption correction with SADABS.[16] CCDC 182/876.

¶ As the chemical shifts in the ^{31}P NMR spectra of alkali metal phosphanides are dependent on concentration, saturated solutions were always used for NMR spectroscopy. Apparently, the solid-state structure is not retained in solution, but discrete anions (and, by inference, cations) are formed.

1 *Organophosphorus Chemistry*, Royal Society of Chemistry, vol. 1–24; E. Hey-Hawkins, *Chem. Rev.*, 1994, **94**, 1661.

2 E. Hey-Hawkins and S. Kurz, *Phosphorus Sulfur Silicon*, 1994, **90**, 281; M. Drieß, H. Pritzkow, S. Martin, S. Rell, D. Fenske and G. Baum, *Angew. Chem.*, 1996, **108**, 1064; M. Drieß, S. Rell, H. Pritzkow and R. Janoschek, *Chem. Commun.*, 1996, 305; G. Becker, B. Eschbach, O. Mundt and N. Seidler, *Z. Anorg. Allg. Chem.*, 1994, **620**, 1381; Review: F. Pauer and P. P. Power, *Structures of Lithium Salts of Heteroatom Compounds*, in *Lithium Chemistry: A Theoretical and Experimental Overview*, ed. A.-M. Sapse and P. v. R. Schleyer, Wiley, New York, 1994, ch. 9, p. 361 and references therein.

3 (a) M. Andrianarison, D. Stalke and U. Klingebiel, *Chem. Ber.*, 1990, **123**, 71; (b) G. A. Koutsantonis, P. C. Andrews and C. L. Raston, *J. Chem. Soc., Chem. Commun.*, 1995, 47; (c) H. C. Aspinall and M. R. Tillotson, *Inorg. Chem.*, 1996, **35**, 5; (d) M. Drieß, G. Huttner, N. Knopf, H. Pritzkow and L. Zsolnai, *Angew. Chem.*, 1995, **107**, 354.

4 M. Drieß, H. Pritzkow, M. Skipinski and U. Winkler, *Organometallics*, 1997, **16**, 5108.

5 G. W. Rabe, G. P. A. Yap and A. L. Rheingold, *Inorg. Chem.*, 1997, **36**, 1990.

6 T. Oshikawa and M. Yamashita, *Chem. Ind. (London)*, 1985, 126.

7 E. Hey and F. Weller, *J. Chem. Soc., Chem. Commun.*, 1988, 783.

8 M. C. Fermin, J. Ho and D. W. Stephan, *J. Am. Chem. Soc.*, 1994, **116**, 6033.

9 M. C. Fermin, J. Ho and D. W. Stephan, *Organometallics*, 1995, **14**, 4247.

10 F. Paul, D. Carmichael, L. Ricard and F. Mathey, *Angew. Chem.*, 1996, **108**, 1204.

11 H.-J. Gosink, F. Nief, L. Ricard and F. Mathey, *Inorg. Chem.*, 1995, **34**, 1306.

12 H. G. von Schnering and W. Hönle, *Z. Anorg. Allg. Chem.*, 1979, **456**, 194; *Chem. Rev.*, 1988, **88**, 243.

13 C. J. Schaverien and J. B. Van Mechelen, *Organometallics*, 1991, **10**, 1704.

14 B. Werner, T. Kräuter and B. Neumüller, *Organometallics*, 1996, **15**, 3746 and references therein.

15 SHELXTL PLUS, Siemens Analyt. X-ray Inst. Inc., 1990, XS: Program for Crystal Structure Solution, XL: Program for Crystal Determination, XP: Interactive Molecular Graphics.

16 R. H. Blessing, *Acta Crystallogr., Sect. A*, 1995, **51**, 33.

Received in Basel, Switzerland, 23rd February 1998; 8/01495G