DALTON
FULL PAPER

Syntheses and solid-state structures of [{K(THF)$_2$(PHTipp)K(THF)(μ-THF)(PHTipp)}$_x$]$_2$ and [Rb(THF)(PHTipp)]$_x$ (Tipp = 2,4,6-Pr$^i_3$C$_6$H$_2$)

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MPHTipp (M = K, Rb; Tipp = 2,4,6-Pr$^i_3$C$_6$H$_2$), prepared from potassium or rubidium and PH$_2$Tipp in toluene heated to reflux, crystallises from THF/pentane as [{K(THF)$_2$(PHTipp)K(THF)(μ-THF)(PHTipp)}$_x$]$_2$ (**1**) and [Rb(THF)(PHTipp)]$_x$ (**2**). The K salt shows a novel helical arrangement of K and P atoms in which THF molecules bridge two helices, while the Rb salt exhibits a ladder-type arrangement of Rb and P atoms.

1 Introduction

While lithium phosphanides have been widely employed as phosphanide-transfer reagents,[1] their heavier congeners have remained largely unexplored.[2,3] Furthermore, most structural studies have focussed on the solid-state structures of lithium phosphanides,[4] and the structures of the heavier alkali metal analogues have only recently been studied.[2,3] A number of examples of sodium,[5–9] potassium,[5a,7,9–16] rubidium[14,17,18] and caesium phosphanides[6,14,17,18] have been reported,[2,3] most of which, like the majority of lithium phosphanides, exhibit dimeric M$_2$P$_2$ arrangements,[5b,d,6] polymeric one-dimensional ladders[10,12,14,17] consisting of alternating M–P and P–M steps, or infinite chains.[6] Lithium phosphanides also form one-dimensional polymeric zigzag[19] or helical[20–22] –M–P–M–P– chains. We recently reported a novel structural type for [K$_3$(THF)$_2$(PHMes)$_3$]$_x$ (Mes = 2,4,6-Me$_3$C$_6$H$_2$),[11] which is the first example of a potassium phosphanide with a polyhedral arrangement of K and P atoms. Here, 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. [K(diox)$_2$PPh$_2$]$_x$ (diox = 1,4-dioxane) forms a three-dimensional network, in which each K ion is surrounded by four bridging dioxane molecules in a plane, and the P atom of the PPh$_2$ anion occupies an axial position. Additionally, π interaction between the K ion and an aryl ring of a PPh$_2$ anion of a neighbouring plane is observed.[16]

In our studies on potential phosphinidene (PR) precursors, we are interested in the synthesis and solid-state structures of PH functionalised alkali metal phosphanides, MPHR. We now report the syntheses and solid-state structures of [{K(THF)$_2$(PHTipp)K(THF)(μ-THF)(PHTipp)}$_x$]$_2$ (**1**) and [Rb(THF)(PHTipp)]$_x$ (**2**) (Tipp = 2,4,6-Pr$^i_3$C$_6$H$_2$).

2 Experimental

All experiments were carried out under purified dry argon. Solvents were dried and freshly distilled under argon. The NMR spectra of saturated solutions were recorded with an AVANCE DRX 400 spectrometer (Bruker), ^{1}H NMR: internal standard solvent (benzene), external standard SiMe$_4$; ^{13}C NMR: external standard SiMe$_4$, internal standard solvent; ^{31}P NMR: external standard 85% H$_3$PO$_4$. The IR spectra were recorded on an FT-IR spectrometer Perkin-Elmer System 2000 in the range 350–4000 cm^{-1}. The melting points were determined in sealed capillaries under argon and are uncorrected.

Preparations

KPHTipp. At room temperature, PH$_2$Tipp (6.7 ml, ρ 0.9 g ml^{-1}, 6.1 g, 25.63 mmol) was added dropwise to a mixture of K (1 g, 25.6 mmol) and THF (50 ml). Then the reaction mixture was heated to reflux for 24 h. The solvent was evaporated *in vacuo*, and the resulting yellow solid washed with hexane (2 × 20 ml) and dried *in vacuo*. Yield: 5.3 g (87%). Mp 205 °C (decomp.). ^{1}H NMR (d$_8$-THF): δ 1.37 (d, 6 H, $^3J_{HH}$ 6.85 Hz, CH$_3$ of *p*-Pr^i), 1.41 (d, 12 H, $^3J_{HH}$ 6.85 Hz, CH$_3$ of *o*-Pr^i), *ca.* 2.4 (d, 1 H, PH), 2.87 (m, 2 H, $^3J_{HH}$ 6.85 Hz, CH of *o*-Pr^i), 3.06 (m, 1 H, $^3J_{HH}$ 6.85 Hz, CH of *p*-Pr^i), 6.80 (s, 2 H, aryl). ^{13}C NMR (d$_8$-THF): δ 23.9 (s, CH$_3$ of *o*-Pr^i), 24.9 (s, CH$_3$ of *p*-Pr^i), 34.9 (CH of *o*-Pr^i), 35.2 (s, CH of *p*-Pr^i), *ca.* 118.8 (s, *m*-C, aryl), *ca.* 145.8 (s, *o*-C, aryl). The linewidths at half height of the signals in the ^{31}P NMR spectrum and of the PH signal in the ^{1}H NMR spectrum, as well as those of the signals of the aryl ring in the ^{13}C NMR spectrum, are large (*e.g.*, 112 Hz in the ^{31}P NMR spectrum). Hence, the signals of the *ipso*-C and *p*-C atoms of the aryl ring are not observed. Assignment of the signals in the ^{13}C NMR spectrum was based on (H,C)-2D experiments. ^{31}P NMR (THF, C$_6$D$_6$): δ −155.5 (d, $^1J_{PH}$ 167 Hz). IR (KBr): 2298 cm^{-1} (νPH).

[{K(THF)$_2$(PHTipp)K(THF)(μ-THF)(PHTipp)}$_x$]$_2$ (1). KPHTipp (2 g) was extracted with THF (50 ml). The resulting solution was concentrated to 10 ml and kept at −22 °C. Yellow crystals of **1** formed overnight, which dissolve again at r.t.

RbPHTipp. At room temperature PH$_2$Tipp (3.2 ml, ρ 0.9 g ml^{-1}, 2.85 g, 12 mmol) was added dropwise to a mixture of 1 g (11.6 mmol) Rb and 50 ml THF. Then the reaction mixture was heated to reflux for 24 h. The solvent was evaporated *in vacuo*, and the resulting yellow solid washed with hexane (2 × 20 ml) and dried *in vacuo*. Yield: 3.2 g (87%). Mp 172–186 °C (decomp.).

[Rb(THF)(PHTipp)]$_x$ (2). Rodlike yellow single crystals of **2** were obtained on concentrating the PH$_2$Tipp–Rb–THF reaction solution to half its volume and layering with 10 ml of pentane after 2 weeks. ^{1}H NMR (d$_8$-THF): δ 1.09 (d, 6 H, CH$_3$ of *p*-Pr^i), 1.14 (d, 12 H, CH$_3$ of *o*-Pr^i), 2.60 (m, 1 H, CH of

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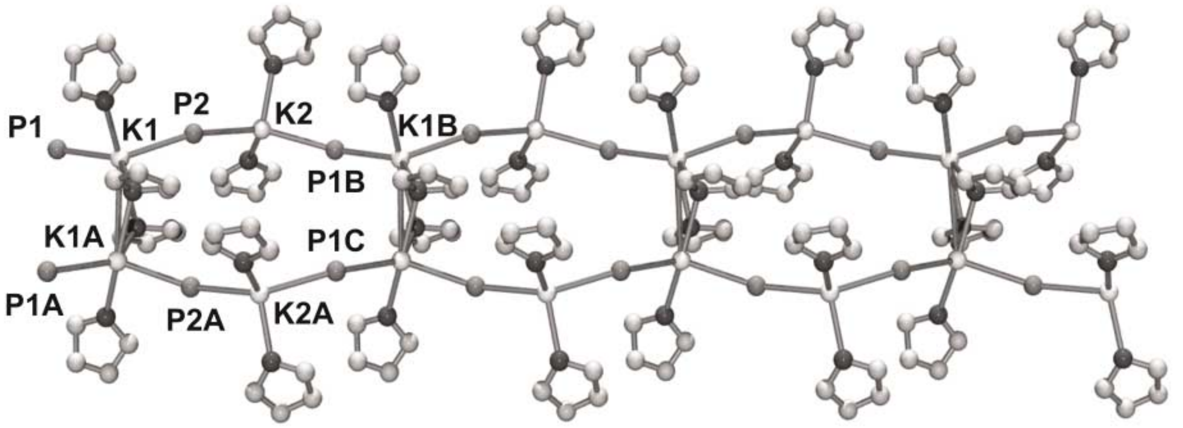

Fig. 1 Section of the polymeric chains in **1** (H atoms and Tipp substituents omitted for clarity; only one position of the disordered THF molecules is shown).

Table 1 Crystal data and structure refinement for **1** and **2**

	1	**2**
Formula	$C_{46}H_{80}K_2O_4P_2$	$C_{38}H_{64}O_2P_2Rb_2$
M_r	837.24	785.77
Crystal system	Monoclinic	Triclinic
a/Å	34.9726(10)	13.165(3)
b/Å	11.5969(3)	13.643(3)
c/Å	28.4498(9)	13.807(3)
α/°	90	113.61(3)
β/°	115.202(2)	103.67(3)
γ/°	90	91.66(3)
V/Å^3	10440.2(5)	2186.6(8)
T/K	213(2)	213(2)
Space group	$C2/c$ (no. 15)	$P\bar{1}$ (no. 2)
Z	8	2
μ/mm^{-1}	0.278	2.338
Refl. collected	20635	19667
Indep. refl.	8443	9166
R_{int}	0.0477	0.0474
R ($I > 2\sigma(I)$)	0.0825	0.0529
$wR2$ (all data)	0.1542	0.1865

p-Pr^i), 6.51 (s, 2 H, aryl); the signals of the CH group of o-Pr^i and of the PH group are not observed. ^{13}C NMR (d_8-THF): δ 21.77 (s, CH_3 of o-Pr^i), 22.94 (s, CH_3 of p-Pr^i), 30.77 (d, $^3J_{PC}$ 15.0 Hz, CH of o-Pr^i), 33.10 (s, CH of p-Pr^i), 116.84 (s, m-C, aryl), 133.80 (s, p-C, aryl), 143.4 (s, o-C, aryl), 152.7 (s, *ipso*-C, aryl); no P–C coupling is observed. ^{31}P NMR (d_8-THF): δ −147.8 (d, $^1J_{PH}$ 154 Hz). IR (KBr): 2294 cm^{-1} (νPH).

Data collection and structure refinement of 1 and 2

Crystallographic details are given in Table 1. Data [λ(Mo-Kα) = 0.71073 Å] were collected with a Siemens CCD (SMART) diffractometer. All observed reflections were used for determination of the unit cell parameters. Empirical absorption correction with SADABS.[23] The structures were solved by direct methods (SHELXTL PLUS[24]). Restrictions for **1** and **2**: K, Rb, P, O, and C atoms anisotropic, H atoms in calculated positions and refined isotropically.

CCDC reference numbers 165077 and 165078.

See http://www.rsc.org/suppdata/dt/b1/b104576h/ for crystallographic data in CIF or other electronic format.

3 Results and discussion

Synthesis of [{K(THF)$_2$(PHTipp)K(THF)(μ-THF)(PHTipp)}$_x$]$_2$ (1) and [Rb(THF)(PHTipp)]$_x$ (2)

The alkali metals K and Rb react with PH_2Tipp in THF heated to reflux to give the alkali metal phosphanides MPHTipp, which are insoluble in toluene or pentane and sparingly soluble in diethyl ether, but dissolve rapidly in THF. The proton-coupled ^{31}P NMR spectra in THF exhibit doublets at δ −155.5 (K) and −147.8 (Rb), which are shifted to low field relative to PH_2Tipp (δ −158.2),[25] and the $^1J_{PH}$ coupling constants of 167 (M = K) and 154 Hz (M = Rb) are smaller than that of PH_2Tipp (203 Hz). 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 structures (see below) are not retained in solution, but discrete anions (and, by inference, cations) are formed.

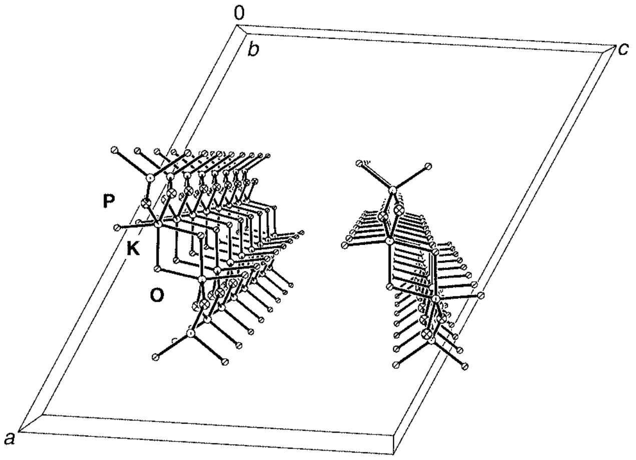

Fig. 2 Unit cell of **1** (only K, P, and O atoms are shown).

Molecular structures of [{K(THF)$_2$(PHTipp)K(THF)(μ-THF)(PHTipp)}$_x$]$_2$ (1) and [Rb(THF)(PHTipp)]$_x$ (2)

Yellow crystals of **1** (needles) and **2** (rodlike) were obtained from THF. Complex **1** crystallises in the monoclinic space group $C2/c$. The asymmetric unit contains two types of potassium and phosphorus atoms. Translation of the crystallographically independent K and P atoms along the y axis and reflection in the crystallographic mirror plane (y = 1/2) results in two infinite polymeric helical chains of alternating K and P atoms that are linked by bridging THF molecules and which have opposite senses of rotation (Fig. 1). The helices are wound around a pseudo 2_1 axis on which the P atoms are located. As the space group is centrosymmetric, a second pair of helices linked by THF molecules is present in the unit cell (Fig. 2).

Each P atom is coordinated to two K atoms, a proton and the Tipp substituent and thus has a coordination number of four. The two K atoms have different coordination numbers; K(1) is coordinated by three THF molecules (one terminal, two bridging THF) and two P atoms, and K(2) has a coordination

Table 2 Selected bond lengths (Å) and angles (°) in **1**

K(1)–P(1)	3.315(2)	K(1)–P(2)	3.314(2)
K(2)–P(1B)	3.269(2)	K(2)–P(2)	3.253(2)
K–O(1)	2.837(3)	K(1)–O(1A)	2.795(3)
K(1)–O(2)	2.662(4)	K(2)–O(3)	2.668(4)
K(2)–O(4)	2.658(4)		
P(1)–K(1)–P(2)	122.31(4)	K(2)–P(1)–K(1)	162.31(5)
K(2)–P(1B)–K(1B)	157.15(5)	P(2)–K(2)–P(1B)	133.47(5)
K(1)–O(1)–K(1A)	100.63(9)		

number of four. The K–P distances in **1** range from 3.314(2) to 3.269(2) Å and are comparable to those in $[\mathrm{KPHMes^*}]_x$ [Mes* = 2,4,6-Bu$^t_3$C$_6$H$_2$, K–P 3.271(2), 3.181(2), 3.357(2) Å],[10] $[\mathrm{K(THF)P(SiMe_3)_2}]_x$ [K–P 3.3169(7), 3.4063(8), 3.4272(8) Å][14] and $[(\mathrm{KPBu^tPh})_2(\mathrm{L})]_x$ [L = THF, py, *N*-methylimidazole (*N*-MeIm); K–P 3.232(3)–3.834(4) Å],[12] which, however, have infinitely extended ladder structures; the related tetrameric compound $[\mathrm{KPH(dmp)}]_4$ [dmp = 2,6-dimesitylphenyl; K–P 3.043(2)–3.438(2) Å],[13] the dimeric compound $[\mathrm{K(THF)_2PMes(SiFBu^t_2)}]_2$ [K–P 3.230(1) Å],[5a] the polymeric compounds $[\mathrm{K_3(THF)_2(PHMes)_3}]_x$ [K–P 3.306(2) to 3.451(1) Å][11] and $[\mathrm{K(diox)_2PPh_2}]_x$ [K–P 3.510(1) Å][16] and in related structures.[7,26–28] In the solid-state compound KP, a polymeric helical chain of P atoms $[^1_\infty\,(\mathrm{P^-})]$ is surrounded by K atoms at short distances of 3.08 to 3.39 Å, and longer distances of 3.62 to 3.86 Å.[29]

While infinite helices have been observed as structural motifs for lithium phosphanides, *e.g.*, $[\mathrm{Li(THF)_2PHMes}]_x$,[21] this is the first potassium phosphanide with a helical arrangement of M and P atoms. Furthermore, bridging THF molecules are rare[30] and have only once been observed in the structures of alkali metal phosphanides.[17] The K–O distances of the bridging THF molecules [K–O(1) 2.837(3), K(1)–O(1A) 2.795(3) Å] are larger than those of the terminal THF molecules at K(1) and K(2) [K(1)–O(2) 2.662(4), K(2)–O(3) 2.668(4), K(2)–O(4) 2.658(4) Å] (Table 2). Bridging THF molecules were also observed in the molecular structure of tetrameric sodium and potassium fluorenone ketyl $[\mathrm{Na_4(OC_{13}H_8)_2(THF)_2(\mu\text{-}THF)_2(OC_{13}H_8)_4}]$ and $[\mathrm{K_4(HMPA)_4(\mu\text{-}THF)(OC_{13}H_8)_4}]$ (HMPA = OP(NMe$_2$)$_3$) [K–O 3.922(15) and 3.007(15) Å].[30]

No π interaction between the aryl substituents and K atoms is observed in **1**, although K–aryl interaction was observed in $[\mathrm{KPHMes^*}]_x$, which is obtained solvent-free even on crystallisation from THF/toluene,[10] as well as in the donor adducts $[(\mathrm{KPBu^tPh})_2(\mathrm{L})]_x$ (L = THF, py, *N*-MeIm)[12] and $[\mathrm{K_3(THF)_2(PHMes)_3}]_x$.[11] Similarly, π coordination of arene ligands to potassium[28,31] and the heavier alkali metals[32] has often been reported.

Compound **2** crystallises in the triclinic centrosymmetric space group $P\bar{1}$. The asymmetric unit, which contains two types of potassium and phosphorus atoms, can be regarded as a dimer of [Rb(THF)PHTipp]. This Rb$_2$P$_2$ four-membered ring has a butterfly structure. Due to a centre of inversion, this Rb$_2$P$_2$ unit generates an infinite ladder with alternating Rb–P and P–Rb steps. The ladder is formed from butterfly-type four-membered rings, which alternate with planar four-membered rings; the middle of this Rb$_2$P$_2$ unit is the centre of inversion (Figs. 3 and 4). The bond angles inside the butterfly-type rings Rb(1)–P(1)–Rb(2)–P(2) are *ca.* 81° at the P atoms and larger (*ca.* 93°) at the Rb atoms [P(1)–Rb(2)–P(2) 93.38(5), P(2)–Rb(1)–P(1) 92.71(5), Rb(1)–P(2)–Rb(2) 81.16(5), Rb(2)–P(1)–Rb(1) 81.51(5)°], while those of the centrosymmetric planar rings Rb(1)–P(2)–Rb(1A)–P(2A) have larger angles (*ca.* 98°) at Rb atoms [P(2)–Rb(1)–P(2A) 81.79(5), Rb(1A)–P(2)–Rb(1) 98.21(5)°] (Table 3).

Table 3 Selected bond lengths (Å) and angles (°) in **2**

Rb(1)–P(1)	3.840(2)	Rb(1)–P(2)	3.459(2)
Rb(1)–P(2A)	3.414(2)	Rb(2)–P(1)	3.423(2)
Rb(2)–P(2)	3.834(2)	Rb(2)–P(1B)	3.413(2)
Rb(1)–O(2)	2.883(5)	Rb(2)–O(1)	2.906(5)
Rb(1)–C(9)	3.116(4)	Rb(1)–C(10)	3.253(5)
Rb(1)–C(11)	3.493(5)	Rb(1)–C(12)	3.645(5)
Rb(1)–C(13)	3.551(5)	Rb(1)–C(14)	3.328(5)
Rb(2)–C(24)	3.266(5)	Rb(2)–C(25)	3.518(5)
Rb(2)–C(26)	3.659(6)	Rb(2)–C(27)	3.571(6)
Rb(2)–C(28)	3.333(5)	Rb(2)–C(29)	3.133(4)
P(1)–C(9)	1.820(5)	P(2)–C(29)	1.824(5)
P(1)–Rb(2)–P(2)	93.38(5)	Rb(2)–P(1)–Rb(1)	81.51(5)
Rb(1)–P(2)–Rb(2)	81.16(5)	P(2)–Rb(1)–P(1)	92.71(5)
P(2A)–Rb(1)–P(2)	81.79(5)	P(2A)–Rb(1)–P(1)	141.47(4)
P(1B)–Rb(2)–P(2)	142.77(4)	Rb(2B)–P(1)–Rb(2)	106.05(5)
Rb(2B)–P(1)–Rb(1)	166.17(5)	Rb(1A)–P(2)–Rb(1)	98.21(5)
Rb(1A)–P(2)–Rb(2)	165.32(6)	P(1B)–Rb(2)–P(1)	73.95(5)
O(1)–Rb(2)–P(1)	91.3(1)	O(1)–Rb(2)–P(2)	120.6(1)
O(2)–Rb(1)–P(2)	86.4(1)	O(2)–Rb(1)–P(1)	116.0(1)
O(2)–Rb(1)–P(2A)	101.8(1)	O(1)–Rb(2)–P(1B)	95.0(1)

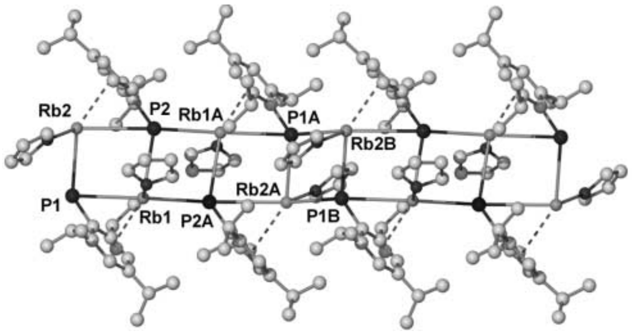

Fig. 3 Section of the infinite ladder structure of **2** (H atoms omitted for clarity).

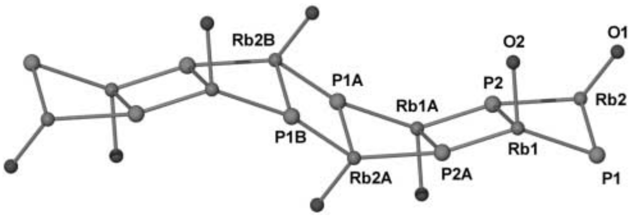

Fig. 4 Section of the ladder structure of **2** (side view); only Rb, P, and O atoms are shown.

Each P atom is surrounded by three Rb atoms and *vice versa*. Thus, the P atoms are five-coordinate. To each Rb atom, a THF molecule is coordinated, and additionally, π interaction (η^6) of the aryl substituent of the neighbouring P atom with Rb is observed [Rb–C$_{\mathrm{aryl}}$ 3.116(4) to 3.659(6) Å] (Fig. 3). Due to this Rb–aryl interaction, the corresponding Rb–P distance is larger than those of the other Rb–P bonds [Rb(1)–P(1) 3.840(2), Rb(2)–P(2) 3.834(2) Å]. The other Rb–P distances [3.413(2) to 3.459(2) Å] are in the range also observed in the puckered ladder structure of $[\mathrm{Rb(THF)P(SiMe_3)_2}]_x$ [Rb–P 3.416(1), 3.484(2), 3.486(2) Å][14] and $[\mathrm{RbPHMes^*}]_x$ [Rb–P 3.381(1), 3.433(1), 3.504(1) Å],[10] the cube-like $[\mathrm{RbPH(dmp)}]_4$ [Rb–P 3.399(2)–3.756(2) Å],[18] and the rubidium phosphide Rb$_4$P$_6$ [Rb–P 3.476(4) to 3.543(4) Å].[33] The overall structure of **2** is very similar to that of the solvent-free compound $[\mathrm{RbPHMes^*}]_x$.[10]

Ladder-type structures have already been observed for the rubidium phosphanides $[\mathrm{Rb(THF)P(SiMe_3)_2}]_x$[14] and $[\mathrm{RbPHMes^*}]_x$,[10] as well as for other alkali metal phosphanides, *e.g.* infinite ladders in $[\mathrm{Li(THF)PHCy}]_x$[34] and $[(\mathrm{KPBu^tPh})_2(\mathrm{L})]_x$ (L = THF, py, *N*-MeIm),[12] four-rung ladders in $[\mathrm{Li_4(THF)_2(PR_2)_4}]$ (R = Bu^t,[35] SiMe$_3$[36]) and $[\mathrm{KPH(dmp)}]_4$,[13] and a six-rung ladder in solvent-free $[\mathrm{LiP(SiMe_3)_2}]_6$,[37] and were also observed in lithium amide chemistry.[38] The solvent-free complexes $[\mathrm{MPHMes^*}]_x$ (M = K, Rb, Cs) have ladder-type structures similar to that of **2**.[10] Here, the base adducts also crystallise as ladder-type polymers, but the type of ladder is dependent on the donor solvent present.

4 Conclusion

Even though K and Rb are larger than Li, the same structural motifs are observed. However, the heavier alkali metals often interact with aryl substituents to increase their coordination number. Apparently, the alkali metal and the steric and electronic properties of the substituents at P determine the structural motif observed. Thus, the three structurally characterised KPHR compounds $[KPH(dmp)]_4$,[13] $[KPHMes^*]_x$,[10] and $[K_3(THF)_2(PHMes)_3]_x$[11] were all crystallised from THF but all have different structures. The potassium salt $[K(THF)_2PHTipp]_x$ described here has a helical structure unprecedented for potassium phosphanides.

While most Rb phosphanides were shown to exhibit the same structural motif as the corresponding K phosphanides ($[MPHMes^*]_x$, M = K, Rb, Cs: ladder-type structures with multihapto interactions between the aryl rings and alkali metal ion;[10] $[M(THF)P(SiMe_3)_2]_x$, M = K, Rb, Cs: ladder-type structures, K and Rb compound isotypic[14]), here a different structure is observed for related phosphanides (helix *versus* ladder). The only other example where K, Rb, and Cs salts have different structures was observed for the compounds MPH(dmp), of which the K salt is tetrameric and forms a four-rung ladder,[13] the Rb salt has a cube-like arrangement of Rb and P atoms, and the Cs salt forms an ion pair of formula $[[Cs_2\{PH(dmp)\}_3{}^-Cs^+]\cdot\frac{1}{3}toluene]$.[18]

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References

1 (*a*) *Organophosphorus Chemistry*, Royal Society of Chemistry, Cambridge, 1970–2001, vol. 1–31; (*b*) E. Hey-Hawkins, *Chem. Rev.*, 1994, **94**, 1661.

2 K. Izod, *Adv. Inorg. Chem.*, 2000, **50**, 33.

3 J. D. Smith, *Angew. Chem., Int. Ed.*, 1998, **37**, 2071.

4 F. Pauer and P. P. Power, *Structures of Lithium Salts of Heteroatom Compounds*, in *Lithium Chemistry: A Theoretical and Experimental Overview*, Eds. A.-M. Sapse and P. v. R. Schleyer, Wiley, New York, 1994, ch. 9, p. 361 and refs. therein.

5 (*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*) M. Drieß, G. Huttner, N. Knopf, H. Pritzkow and L. Zsolnai, *Angew. Chem.*, 1995, **107**, 354; M. Drieß, G. Huttner, N. Knopf, H. Pritzkow and L. Zsolnai, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 316; (*d*) H. C. Aspinall and M. R. Tillotson, *Inorg. Chem.*, 1996, **35**, 5.

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

7 F. Paul, D. Carmichael, L. Ricard and F. Mathey, *Angew. Chem.*, 1996, **108**, 1204; F. Paul, D. Carmichael, L. Ricard and F. Mathey, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 1125.

8 O. Kühl, J. Sieler, G. Baum and E. Hey-Hawkins, *Z. Anorg. Allg. Chem.*, 2000, **626**, 605.

9 W. Clegg, S. Doherty, K. Izod, H. Kagerer, P. O'Shaughnessy and J. M. Sheffield, *J. Chem. Soc., Dalton Trans.*, 1999, 1825.

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

11 C. Frenzel, P. Jörchel and E. Hey-Hawkins, *Chem. Commun.*, 1998, 1363.

12 G. W. Rabe, S. Kehradmandan, H. Heise, I. A. Guzei, L. M. Liable-Sands and A. L. Rheingold, *Main Group Chem.*, 1998, **2**, 221.

13 G. W. Rabe, S. Kehradmandan and G. P. A. Yap, *Inorg. Chem.*, 1998, **37**, 6541.

14 U. Englich, K. Hassler, K. Ruhlandt-Senge and F. Uhlig, *Inorg. Chem.*, 1998, **37**, 3532.

15 M. A. Beswick, A. D. Hopkins, L. C. Kerr, M. E. G. Mosquera, J. S. Palmer, P. R. Raithby, A. Rothenberger, D. Stalke, A. Steiner, A. E. H. Wheatley and D. S. Wright, *Chem. Commun.*, 1998, 1527.

16 O. Kühl, J. Sieler and E. Hey-Hawkins, *Z. Kristallogr.*, 1999, **214**, 496.

17 G. W. Rabe, H. Heise, G. P. A. Yap, L. M. Liable-Sands, I. A. Guzei and A. L. Rheingold, *Inorg. Chem.*, 1998, **37**, 4235.

18 G. W. Rabe, S. Kehradmandan, L. M. Liable-Sands, I. A. Guzei and A. L. Rheingold, *Angew. Chem.*, 1998, **110**, 1495; G. W. Rabe, S. Kehradmandan, L. M. Liable-Sands, I. A. Guzei and A. L. Rheingold, *Angew. Chem., Int. Ed.*, 1998, **37**, 1404.

19 (*a*) R. A. Bartlett, M. Olmstead and P. P. Power, *Inorg. Chem.*, 1986, **25**, 1243; (*b*) R. A. Jones, S. U. Koschmieder and C. M. Nunn, *Inorg. Chem.*, 1987, **26**, 3610; (*c*) G. Becker, H.-M. Hartmann and W. Schwarz, *Z. Anorg. Allg. Chem.*, 1989, **577**, 9.

20 G. Stieglitz, B. Neumüller and K. Dehnicke, *Z. Naturforsch., Teil B*, 1993, **48**, 156.

21 E. Hey and F. Weller, *J. Chem. Soc., Chem. Commun.*, 1988, 782.

22 G. Becker, B. Eschbach, O. Mundt and N. Seidler, *Z. Anorg. Allg. Chem.*, 1994, **620**, 1381.

23 G. M. Sheldrick, SADABS, a Program for Empirical Absorption Correction, Göttingen, 1998.

24 SHELXTL PLUS, Siemens Analytical X-ray Instruments Inc., 1990, XS: Program for Crystal Structure Solution, XL: Program for Crystal Structure Determination, XP: Interactive Molecular Graphics.

25 S. Kurz, PhD thesis, Universität Leipzig, 1994.

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

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

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

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

30 (*a*) Z. Hou, X. Jia, A. Fujita, H. Tezuka, H. Yamazaki and Y. Wakatsuki, *Chem. Eur. J.*, 2000, **6**, 2994; (*b*) Z. Hou, A. Fujita, H. Yamazaki and Y. Wakatsuki, *Chem. Commun.*, 1998, 669; (*c*) S. Brooker, F. T. Edelmann, T. Kottke, H. W. Roesky, G. M. Sheldrick, D. Stalke and K. H. Whitmire, *J. Chem. Soc., Chem. Commun.*, 1991, 144; (*d*) Q. Shen, M. Qi and Y. Lin, *J. Organomet. Chem.*, 1990, **399**, 247.

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

32 B. Werner, T. Kräuter and B. Neumüller, *Organometallics*, 1996, **15**, 3746 and refs. therein.

33 H. G. von Schnering, T. Meyer, W. Hönle, W. Schmettow, U. Hinze, W. Bauhofer and G. Kliche, *Z. Anorg. Allg. Chem.*, 1987, **553**, 261.

34 E. Hey-Hawkins and S. Kurz, *Phosphorus, Sulfur Silicon Relat. Elem.*, 1994, **90**, 281.

35 R. A. Jones, A. L. Stuart and T. C. Wright, *J. Am. Chem. Soc.*, 1983, **105**, 7459.

36 E. Hey, P. B. Hitchcock, M. F. Lappert and A. K. Rai, *J. Organomet. Chem.*, 1987, **325**, 1.

37 E. Hey-Hawkins and E. Sattler, *J. Chem. Soc., Chem. Commun.*, 1992, 775.

38 R. E. Mulvey, *Chem. Soc. Rev.*, 1991, **20**, 167.