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Synthesis and X-ray Crystal Structure Determination of the First Potassium Salt of a Primary Phosphane: [KP(H)Mes*]$_x$

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"Supermesitylphosphane" [i.e. (2,4,6-^{t}Bu$_3$C$_6$H$_2$)PH$_2$ = Mes*-PH$_2$][1] has been widely used during the past years as a sterically demanding, phosphorus-containing ligand both in main-group[2] and in transition-metal chemistry.[3] The main transfer reagent typically employed was either the lithium salt Mes*P(H)Li·3THF[3] or the phosphane itself.[2] It is noteworthy that only *mono*metalation of Mes*PH$_2$ can be achieved according to earlier reports.[4]

Interestingly, no information is available in the literature on the synthesis, isolation, and characterization of other alkali metal salts of this particular ligand. Here we wish to report the potassium derivative of supermesitylphosphane, thus representing a first report on a heavier alkali metal salt of a *primary* phosphane.

In light of the dearth of structural data[5] available on molecular phosphide species of the heavier alkali metals of the general formula M[PR$_2$] or M[PRH], we were interested in investigating the accessibility as well as structural aspects of the potassium derivative of supermesitylphosphane. This lack of information available on solid-state structures of salts of heavier congeners of alkali metals is rather surprising since several structural studies on lithium phosphides have appeared since the early eighties.[6] These studies have shown that LiPR$_2$ species can exhibit a variety of molecular structures depending on the substituent R on phosphorus and the type of solvent and/or donor ligand D employed. Variation in R and D vastly affects the solid-state structures of these species. The interest in heavier alkali metal salts of phosphides[7] as well as their solid-state structures arises from their synthetic potential as transfer agents as well as fundamental and theoretical aspects. Also, alkali metal salts of [PRH] anions are of interest since they are potential transfer agents toward the formation of complexes that can be used as suitable precursors for generating phosphinidene species of the early transition metals[3] and the actinides.[8]

Reaction of potassium hydride with 1 equiv of supermesitylphosphane in tetrahydrofuran solution at room temperature forms the title complex KP(H)Mes* (**1**) in 80% yield,[9] which was found to be insoluble in hexanes as well as in aromatic solvents.

The molecular structure[10] of the pale yellow potassium derivative **1** has an extended, one-dimensional polymeric ladder-

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(9) Characterization data for **1**: In the glovebox, addition of a solution of supermesitylphosphane (200 mg, 0.72 mmol) in 5 mL of tetrahydrofuran to a colorless suspension of KH (29 mg, 0.72 mmol) in 5 mL of tetrahydrofuran caused a slow color change to yellow. The reaction mixture was stirred for 1 h. Removal of solvent, extraction of the residues with toluene/tetrahydrofuran (2:1), and centrifugation, followed by crystallization at −30 °C and drying under vacuum, gave **1** as yellow crystals (182 mg, 80%). Complex **1** is soluble in tetrahydrofuran. Anal. Calcd for C$_{18}$H$_{30}$KP: C, 68.31; H, 9.55; K, 12.35. Found: C, 68.03; H, 9.67; K, 11.95. ^{1}H NMR (C$_4$D$_8$O, 400 MHz, 25 °C): δ 1.14 (s, 9H), 1.60 (s, 18H), 2.84 (d, $J_{\mathrm{P-H}} = 163$ Hz, 1H), 6.83 (s, 2H). ^{31}P NMR (C$_4$D$_8$O, 161.9 MHz, 25 °C): δ −89.3 (d, $J_{\mathrm{P-H}} = 163$ Hz). ^{13}C NMR (C$_4$D$_8$O, 100.4 MHz, 25 °C): δ 31.3, 31.4, 32.3, 34.7 (CH$_3$−C), 38.8 (CH$_3$−*C*), 120.1 (d, $J = 1.8$ Hz, *meta*-C), 135.4 (d, $J = 1.8$ Hz, *para*-C), 145.8 (d, $J = 6.5$ Hz, *ortho*-C), 158.5 (d, $J_{\mathrm{C-P}} = 78$ Hz, *ipso*-C). IR (Nujol): 2358 vs, 2356 s, 1277 s, 1163 m, 1033 vs, 879 m, 752 m, 721 w, 668 w, 633 w, 594 w cm^{-1}. UV−vis (tetrahydrofuran, $\lambda_{\max}$, nm (ϵ)): 402 (3270), 382 (sh, 2730), 251 (7150), 245 (7660), 237 (7760), 226 (9220).

(10) Crystal data for **1**: C$_{18}$H$_{30}$KP, $M_r = 632.98$, triclinic, $P\bar{1}$, $a = 6.508(1)$ Å, $b = 10.113(2)$ Å, $c = 15.586(2)$ Å, $\alpha = 82.51(1)°$, $\beta = 79.98(2)°$, $\gamma = 75.52(1)°$, $V = 973.9(3)$ Å^3, $Z = 2$, $\rho_{\mathrm{calc}} = 1.079$ g cm^{-3}, $F(000) = 344$, Mo Kα radiation ($\lambda = 0.710\,73$ Å), $T = 233(2)$ K, μ(Mo Kα) = 0.346 mm^{-1}. A total of 3326 reflections were collected on a Siemens P4 diffractometer on a yellow crystal with approximate dimensions 0.40 × 0.40 × 0.20 mm^3 in the range from $4.18° \le 2\theta \le 45.00°$. Of the total, 2530 reflections were independent, and 1713 reflections were considered observed and used for refinement. The structure was solved by direct methods and refined by full-matrix least-squares on F^2 to final residuals of $R_1 = 0.0627$ and w$R_2 = 0.1509$ for 1713 observed data ($I > 2\sigma(I)$) and GOF = 1.050. The function minimized was $R(\mathrm{w}F^2) = \Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[(wF_o^2)^2]^{1/2}$ with $R = \Sigma\Delta/\Sigma(F_o)$ and $\Delta = |(F_o - F_c)|$. The hydrogen atom on phosphorus was located from the difference map, its thermal parameter was fixed, and its coordinates were allowed to refine. Minimal/maximal residual electron density: 0.307/−0.261 e Å^{-3}. All software and sources of scattering factors are contained in the SHELXTL (5.3) program library (G. Sheldrick, Siemens, XRD, Madison, WI). Atomic coordinates, bond distances and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (depository code NALLAN).

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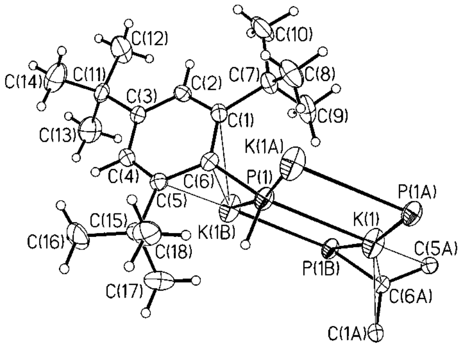

Figure 1. Molecular structure of [KP(H)Mes*]$_x$ (**1**) showing the η^3-coordination of the Mes* ring and three of the K−P rungs of the infinitely extended, centrosymmetric ladder structure. Selected interatomic separations (Å) and angles (deg): P(1)−K(1) = 3.271(2), P(1)−K(1a) = 3.181(2), P(1)−K(1b) = 3.357(2), K(1)−C(6) = 2.884(4), K(1)−C(5) = 3.164(4), K(1)−C(1) = 3.197(4), P(1)−H(1) = 1.20(2); C(6)−P(1)−H(1) = 103(2), K(1)−P(1)−K(1a) = 101.8(1), K(1)−P(1)−K(1b) = 85.7(1), K(1a)−P(1)−K(1b) = 169.0(1)°.

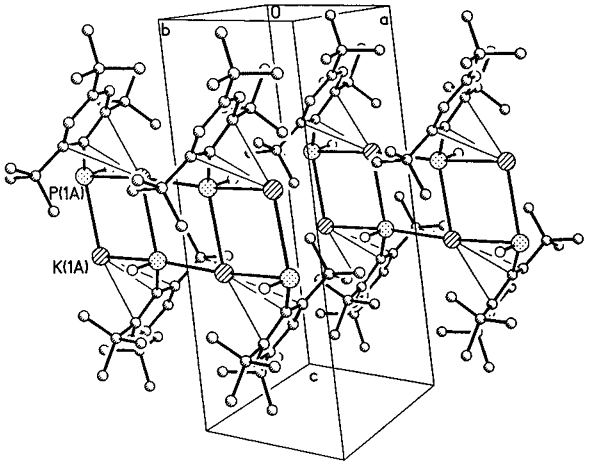

Figure 2. Unit-cell packing diagram for [KP(H)Mes*]$_x$ showing the parallel extensions of the ladder structure.

type connectivity with each phosphorus atom coordinated to three potassium atoms [K−K−K = 86.2(1)°] (Figure 1). Surprisingly, no THF molecule was found in the coordination sphere of the potassium cation although crystals were obtained from a toluene/tetrahydrofuran mixture. Figure 2 shows how the ladders are spatially extended. The three K−P distances in the potassium salt are 3.181(2), 3.271(2), and 3.357(2) Å. These numbers can be compared with the K−P distance of 3.230(1) Å in [^{t}Bu$_2$SiFK(THF)$_2$PC$_6$H$_2$Me$_3$]$_2$[7c] and the corresponding distances in Cp*$_2$ZrP$_3$K(THF)$_{1.5}$ ranging from 3.37(1) to 3.61(1) Å[7f] and in Cp$_2$ZrH[P(C$_6$H$_2$-2,4,6-^{t}Bu$_3$)]K(thf)$_2$ [3.497(9) Å],[7g] as well as the K−P distances in a potassium phospholide system [3.264(1) and 3.256(1) Å].[7d] Each potassium atom, in addition to being likewise coordinated to three phosphorus atoms, appears to be coordinating to the π-cloud of a neighboring supermesityl ring in an approximate η^3 mode with K−C distances of 2.884(4) Å [C(6)], 3.164(4) Å [C(5)], and 3.197(4) Å [C(1)]. The overall molecular structure of the potassium salt can therefore be described as polymeric [KP(H)Mes*]$_x$.

The −P(H)Mes* ligand itself has not been observed earlier acting as a π-donor ligand. However, π-coordination of arene type ligands to the heavier alkali metal cations has precedence in the literature.[11] Apparently, the π-interaction between the potassium cation and the neighboring sterically demanding supermesityl ring in the polymeric structure prevents additional coordination of solvent to the metal center. The superstructure of the [KP(H)Mes*]$_x$ polymer appears like a ribbon of potassium and phosphorus atoms covered with *tert*-butyl moieties. A *nonpolymeric* ladder-type structure with six M−P steps has been reported for solvent-free LiP(SiMe$_3$)$_2$.[6f] Also, the ladder-type connectivity of **1** can be compared with the organonitrogen−lithium laddered structure of a (pyrrolidido)lithium−pentamethyldiethylentriamine (PMDETA) adduct,[12] which is complexed by PMDETA, so preventing further association.

The environment around the phosphorus atom in complex **1** can best be described as a heavily distorted square pyramid with the apical position occupied by a hydrogen atom. This deviation from ideal square pyramidal geometry can be seen by examining the Mes*−C(6)−P(1)−K(1) angle [139.5(1)°] which is found to be quite small. This observation can be rationalized in terms of distortion resulting from additional π-coordination of the supermesityl ring to the next alkali metal cation.

A certain amount of deformation of the phenyl ring is found to be present in the title complex. This deviation from the ideal 180° plane is most readily seen by examining the C−C−C angles of the aromatic substituent ranging from 115.3(3) to 125.2(4)° [with C−C distances ranging from 1.380(5) to 1.445(5) Å]. The deviation from planarity is greatest at C(6), which is elevated 0.105 Å above the plane formed by C(1)−C(5). C(6), in addition to being the *ipso* carbon atom, forms the shortest bond to K(1b) at 2.884(4) Å. Nonplanarity of the supermesityl aryl ring has been observed as well in other systems, presumably resulting from steric hindrance.[13]

The study presented above gives insight into structural aspects of the potassium derivative of supermesitylphosphane, KP(H)-Mes* (**1**), which can be easily prepared and isolated in good yields thus representing a potential transfer reagent for the −P(H)Mes* ligand.

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Supporting Information Available: Tables listing detailed crystallographic data, atomic positional and thermal parameters, and bond lengths and angles (6 pages). Ordering information is given on any current masthead page.

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