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The $(P_4HMes_4)^-$ Anion: Lability, Fluxionality, and Structural Ambiguity ($Mes = 2,4,6\text{-}Me_3C_6H_2$)

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The synthesis and structural characterization of the tetramesityltetraphosphanide anion, $(P_4HMes_4)^-$ (**1**), is described. It is shown that **1** partially decomposes in solution and displays an unsymmetrical structure in which, depending on conditions, the proton may or may not fluctuate between the terminal P atoms of the P_4 chain.

Introduction

Alkali metal oligophosphanediides, $M_2(P_nR_n)$ ($n = 2-4$),[1,2] are versatile reagents and display an intriguing structural chemistry. Thus, it has been shown that they have considerable potential for the synthesis of phosphorus-rich main group and transition metal complexes.[3,4c] Only recently have the structural principles governing this class of compounds been fully unraveled.[4,5] Interestingly, the $(P_nR_n)^{2-}$ dianions are readily protonated, and doubly protonated tetraorganotetraphosphanes, $P_4H_2R_4$, [4c,6] triorganotriphosphanes, $P_3H_2R_3$,[7] and diphosphanes, $P_2H_2R_2$,[6a,8] have been described. In contrast, reports on monoprotonated anions, $(P_nHR_n)^-$, are extremely scarce: the compounds $[K(pmdeta)(P_2HtBu_2)]_2$ [pmdeta = $MeN(CH_2CH_2NMe_2)_2$],[9] $[Li(thf)(P_2HPh_2)]_4$,[10] and $[K(crypt)][P_2HPh_2]$[4b] (crypt = 2,2,2-cryptand) were obtained by protonation of $(P_2tBu_2)^{2-}$ with water,[9] solvolysis of $(P_2R_2)^{2-}$ dianions,[4b,11] and aluminum-mediated coupling of Li(PHPh). [10]

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Very recently, protonated tetraphosphanide anions have emerged as potential building blocks for phosphorus-rich metal complexes. For example, we have reported the structure of $[Cp^{\circ}MoCl_2(P_4HCy_4)]$ ($Cp^{\circ} = C_5Me_4Et$) containing the tetraphosphanide anion $(P_4HCy_4)^-$,[12] the first crystallographic observation of a triphosphanide anion, namely, $(P_3HMes_3)^-$, in the complex $\{K(pmdeta)(P_3HMes_3)\}_2\{K_2(P_4Mes_4)\}]$[5b] (Mes = 2,4,6-$Me_3C_6H_2$), and the serendipitous isolation of the Cu^I complexes $[Cu_2(P_2HMes_2)_2(PCyp_3)_2]$ and $[Cu_5Cl(P_2HMes_2)_3(PHMes)(PCyp_3)_2]$ (Cyp = *cyclo*-C_5H_9).[4c] While these results have allowed some preliminary insights into the coordination behavior of such anions, it must be emphasized that the oligophosphanide anions present in these compounds were formed in a serendipitous fashion, and the chemistry of protonated oligophosphanide anions has thus remained poorly understood. We now report the targeted synthesis and structural characterization of the tetramesityltetraphosphanide anion $(P_4HMes_4)^-$ (**1**), in the form of its potassium salts $[K(18\text{-}crown[6])(thf)_2][P_4HMes_4]$ (Kthf·**1**) and $[K(18\text{-}crown\text{-}[6])(P_4HMes_4)]$ (K·**1**).

Experimental Section

General Procedures. All experiments were performed under an atmosphere of dry argon using standard Schlenk techniques. All solvents were purified by distillation, dried, saturated with argon, and stored over a potassium mirror. NMR and EPR samples were prepared under argon, and the tubes were flame-sealed to exclude oxygen and moisture rigorously. The NMR spectra were recorded on a Bruker AVANCE-DRX-400 spectrometer: ^1H NMR (400.13 MHz) internal standard, solvent; external standard, TMS; and ^{31}P NMR (161.9 MHz) external standard, 85% H_3PO_4. The ^{31}P MAS NMR (202.45 MHz) spectra were recorded with a Bruker MSL 500 spectrometer at a spinning frequency 12 kHz. The EPR spectra were recorded on a Bruker ESP 300e X-band EPR spectrometer ($F \approx 9.5$ GHz). The mesityl resonances in the ^1H NMR spectra of Kthf·**1**, K·**1**, and K·**3** could not be assigned because of the formation of a mixture of products in solution. The ^{31}P NMR parameters of **1** and $(P_3HMes_3)^-$ were obtained by simulation using the program SPINWORKS (Marat, K.; *SPINWORKS*, version 2.3; University of Manitoba: Winnipeg, MB, Canada, 2004). Negative signs were generally used for the $^1J(P-P)$ coupling constants (Finer, E. G.; Harris, R. K. *Mol. Phys.* **1967**, *13*, 65 and Albrand, J. P.; Faucher, H.; Gagnaire, G.; Robert, J. B. *Chem. Phys. Lett.* **1976**, *38*, 521). For the IR spectra, Nujol mulls were prepared in a nitrogen-filled glovebox, and the spectra were recorded on an FTIR spectrometer Perkin-Elmer System 2000 in the range of 350−4000 cm^{-1}. The FT Raman spectra were recorded on polycrystalline chunks sealed in Pyrex capillaries ($d = 2-3$ mm) with a Bruker FRA 106 spectrometer (Nd:YAG Laser 1064 nm, 200 mW). The melting points are uncorrected. $K_2(P_4Mes_4)$ was synthesized according to the literature procedure.[5b] HCl in Et_2O, DCl in Et_2O, and 18-crown-[6] were obtained from commercial sources. 18-crown[6] was dried by vacuum sublimation before use.

Kthf·1. A solution of 0.33 mL (0.7 mmol) of HCl in Et_2O (2 M) in 5 mL of diethyl ether was carefully added to a red solution of 0.45 g (0.7 mmol) of $K_2(P_4Mes_4)$ in 7 mL of THF. An orange suspension formed which was allowed to warm to room temperature slowly over several hours and was stirred overnight. Subsequently, a solution of 0.17 g (0.7 mmol) of 18-crown[6] in 6 mL of THF was added at room temperature, and the deep-red color of the solution intensified. The solvent was reduced to ~3 mL, and the red solution was layered with 10 mL of *n*-hexane. A red solid formed over 2 days at +5 °C, which was isolated and recrystallized from 10 mL of THF. Kthf·**1** crystallizes with one thf molecule of solvation in the lattice per two molecules of **1**. Yield: 0.35 g (46%). mp: 87−91 °C. Anal. Calcd for $C_{58}H_{89}O_{8.5}P_4K$: C, 64.19; H, 8.27; O, 12.53. Found: C, 63.89; H, 8.16; O, 11.96. ^1H NMR (C_6D_6, 25 °C): δ 1.41 (m, 8H, CH_2 of THF), 1.92 (s, CH_3), 2.00 (s, CH_3), 2.06 (s, CH_3), 2.19 (s, CH_3), 2.27 (s, CH_3), 2.31 (s, CH_3), 2.48 (s, CH_3), 2.61 (s, CH_3), 2.80 (s, CH_3), 2.84 (s, CH_3), 3.01 (s, 24H, CH_2 of 18-crown[6]), 3.10 (s, CH_3), 3.57 (m, 8H, CH_2 of THF), 6.50 (s, CH), 6.65 (s, CH), 6.69 (s, CH), 6.73 (s, CH), 6.84 (s, CH), 6.90 (s, CH), 6.96 (s, CH), 7.00 (s, CH), 7.05 (s, CH), 7.35 (s, CH). $^{31}P\{^1H\}$ NMR (C_6D_6, 25 °C): δ −11.3 (br m), −17.0 (br m), −43.6 [s, *cyclo*-(P_4Mes_4)], −83.7 (br m), −84.9 [d, $^1J_{PP} = \pm 385$ Hz, PHMes part of $(P_2HMes_2)^-$], −101.3 (br m), −109.8 [s, $^1J_{PP} = \pm 184.4$ Hz, P_A in *cyclo*-(P_3Mes_3)], −110.9 [s, (R*,R*)-$P_2H_2Mes_2$], −118.1 [s, (R*,S*)-$P_2H_2Mes_2$], −133.5 [d, $^1J_{PP} = \pm 385$ Hz, $(PMes)^-$ part of $(P_2HMes_2)^-$], −144.3 [d, $^1J_{PP} = \pm 184.4$ Hz, P_B in *cyclo*-(P_3Mes_3)]. ^{31}P NMR (THF/$[D_8]$THF (3:1), −100 °C): δ_A −15.9, δ_B −103.86(1) [m, $(P_4HMes_4)^-$ (**1**), AB part of an AA′BB′X spin system, $^1J_{AB} = {}^1J_{A'B'} = -327.8(3)$ Hz, $^1J_{AA'} = -265.3(2)$ Hz, $^2J_{AB'} = {}^2J_{A'B} = +16.2(1)$ Hz, $^3J_{BB'} = -0.1(2)$ Hz, $^1J_{BX} = \pm 108.8(3)$ Hz, $^1J_{AX} = 0.0(3)$ Hz], δ_A −12.38(1), δ_B −94.94, δ_C −111.12(1) [m, (R*,S*)-$(P_3HMes_3)^-$, ABC part of an ABCX spin system, $^1J_{AB} = \pm 140.2(2)$ Hz, $^1J_{AC} = \pm 359.8(2)$ Hz, $^2J_{BC} = \pm 92.6(2)$ Hz, $^1J_{BX} = \pm 204.6(3)$ Hz, $^2J_{AX} = \pm 9.4(3)$ Hz, $^3J_{CX} = \pm 0.0(3)$ Hz],[13] δ_A −28.65(1), δ_B −92.28(1), δ_C −114.33(1) [m, (R*,R*)-$(P_3HMes_3)^-$, ABC part of an ABCX spin system, $^1J_{AB} = \pm 309.2(3)$ Hz, $^1J_{AC} = \pm 359.2(3)$ Hz, $^2J_{BC} = \pm 91.6(3)$ Hz, $^1J_{BX} = \pm 189.6$ Hz],[13] δ −51.8 [s, *cyclo*-(P_4Mes_4)], −101.9 [d, *cyclo*-(P_3Mes_3)], −114.3 [m, (R*,R*)-$P_2H_2Mes_2$, A part of an AA′XX′ spin system], −123.3 [m, (R*,S*)-$P_2H_2Mes_2$, A part of an AA′XX′ spin system], −150.7 [t, *cyclo*-(P_3Mes_3), $^1J_{PP} = \pm 195.5$ Hz], −150.8 [t, $MesPH_2$, $^1J_{PH} = \pm 204.4$ Hz]. In the reaction mixture (THF) or in clear THF solutions of Kthf·**1**, produced by dissolving all of the red solid by gentle heating immediately before measuring the spectrum at room temperature, a strong EPR signal is detected: $g_0 = 2.014979$, $a_0 = 5.0$ mT = 141.01 MHz = 47.0×10^{-4} cm^{-1}. Solutions of Kthf·**1** in C_7D_8, C_6D_6, or saturated THF solutions display no signal or only a very weak one with the same parameters as those in clear THF solutions. IR (Nujol, cm^{-1}): ν 1604 (w), 1351 (m), 1260 (m), 1250 (m), 1108 (s), 1041 (m), 962 (m), 846 (w).

K·1. K·**1** was prepared in a manner similar to Kthf·**1** using 0.52 g (0.77 mmol) of $K_2(P_4Mes_4)$, 0.38 mL (0.77 mmol) of HCl in Et_2O (2 M) and 0.20 g (0.77 mmol) of 18-crown[6]. The crude product obtained from THF/*n*-hexane by the above procedure was recrystallized from 3 mL of toluene. Deep red crystals of K·**1** formed upon storage at −20 °C for several days. The toluene molecules of solvation initially present in the crystals were lost when the compound was dried in high vacuum for at least 1 h. Yield: 0.34 g (48%). mp: 106−107 °C (formation of a red oil). Anal. Calcd for $C_{48}H_{69}O_6P_4K$: C, 63.70; H, 7.68; O, 10.61;

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[13] Details of the assignment of the two diastereomers of (R*,R*)-$(P_3HMes_3)^-$ are given in the Supporting Information. Determination of the J_{PH} couplings of (R*,R*)-$(P_3HMes_3)^-$ by simulation was not possible because of signal overlap. The given NMR parameters (chemical shift and J_{PP} couplings) refer to the analysis of the $^{31}P\{^1H\}$ NMR spectrum (rms = 0.31 Hz). The $^1J_{BX}$ coupling constant was extracted from the ^{31}P NMR spectrum by hand.

Found: C, 63.06; H, 7.09; O, 11.07. ^{1}H NMR (C_7D_8, 25 °C): δ 1.94 (s, CH_3), 2.00 (s, CH_3), 2.05 (s, CH_3), 2.07 (s, CH_3), 2.09 (overlapping s, CH_3), 2.12 (s, CH_3), 2.18 (s, CH_3), 2.23 (s, CH_3), 2.27 (s, CH_3), 2.44 (s, CH_3), 2.52 (s, CH_3), 2.73 (s, CH_3), 2.75 (m, CH_3), 2.94 (s, CH_3), 3.00 (s, CH_3), 3.04 (s, 24H, CH_2 of 18-crown-[6]), 4.1−5.4 (overlapping m, PH), 6.47 (s, CH), 6.63 (s, CH), 6.65 (s, CH), 6.67 (s, CH), 6.77 (s, CH), 6.91 (s, CH), 6.98 (s, CH), 7.01 (s, CH), 7.07 (s, CH), 7.09 (s, CH). $^{31}P\{^1H\}$ NMR (C_7D_8, 25 °C): δ −11.2 (br m), −17.0 (br m), −43.7 [s, *cyclo*-(P_4Mes_4)], −78.3 (d, $J_{PP} = \pm 255.9$ Hz), −82.3 (br m), −84.8 [d, $^1J_{PP} = \pm 384$ Hz, PHMes part of $(P_2HMes_2)^-$], −100.5 (br m), −110.0 [d, $^1J_{PP} = \pm 184.0$ Hz, P_A in *cyclo*-(P_3Mes_3)], −111.0 [s, (R^*,R^*)-$P_2H_2Mes_2$], −118.3 [s, (R^*,S^*)-$P_2H_2Mes_2$], −134.0 [d, $^1J_{PP} = \pm 385$ Hz, $(PMes)^-$ part of $(P_2HMes_2)^-$], −144.3 [t, $^1J_{PP} = \pm 184.9$ Hz, P_B in *cyclo*-(P_3Mes_3)]. ^{31}P NMR (C_7D_8, −80 °C): δ −7.7 (br m), −20.5 (m), −35.5 (m), −37.4 (pseudo-t, $J_{PP} = -343.4$ Hz), −49.2 [s, *cyclo*-(P_4Mes_4)], −86 to −121 (br overlapping m), −148.4 [t, P_B in *cyclo*-(P_3Mes_3), $J_{PP} = \pm 194.3$ Hz]. IR (Nujol, cm^{-1}): ν 1603 (w), 1351 (m), 1250 (w), 1111 (s), 1029 (w), 962 (m), 844 (w).

Kthf·3. Kthf·**3** was synthesized by a procedure analogous to that for Kthf·**1** using 1.24 mL (1.24 mmol) of DCl in Et_2O (1 M), 0.84 g (1.24 mmol) of $K_2(P_4Mes_4)$, and 0.33 g (1.24 mmol) of 18-crown-[6]. Yield: 0.69 g (51%). mp: 89.5−91 °C. Anal. Calcd for $C_{58}H_{88}DO_{8.5}P_4K$: C, 64.11; H, 8.35; O, 12.53. Found: C, 63.48; H, 8.95; O, 12.54. ^{1}H NMR (C_6D_6, 25 °C): δ 1.41 (8H, CH_2 of THF), 1.92 (s, CH_3), 2.00 (s, CH_3), 2.06 (s, CH_3), 2.16 (s, CH_3), 2.20 (s, CH_3), 2.24 (s, CH_3), 2.27 (s, CH_3), 2.32 (s, CH_3), 2.49 (s, CH_3), 2.62 (s, CH_3), 2.79 (s, CH_3), 2.85 (s, CH_3), 2.86 (s, CH_3), 3.01 (s, 24H, CH_2 of 18-crown[6]), 3.11 (s, CH_3), 3.57 (t, 8H, CH_2 of THF), 6.50 (s, CH), 6.65 (s, CH), 6.69 (s, CH), 6.74 (s, CH), 6.82 (s, CH), 6.84 (s, CH), 6.90 (s, CH), 6.93 (s, CH), 7.01 (s, CH), 7.05 (s, CH), 7.35 (s, CH). ^{2}H NMR (C_6D_6, 25 °C): δ 4.3 to ~6.5 (br, partial overlap with the solvent signal). ^{2}H NMR (THF, −100 °C): δ 7.39 [s, $(P_4DMes_4)^-$]. $^{31}P\{^1H\}$ NMR (C_6D_6, 25 °C): δ −9.5 to −12.9 (br m), −15 to −17.5 (br m), −43.7 [s, *cyclo*-(P_4Mes_4)], −83.5 to −86 (br m), −98.8 to −102 (br m), −110.0 [d, $^1J_{PP} = \pm 184.6$ Hz, P_A in *cyclo*-(P_3Mes_3)], −110.0 to −111.5 (br m), −118.2 (br m), −144.5 [t, $^1J_{PP} = \pm 184.6$ Hz, P_B in *cyclo*-(P_3Mes_3)]. $^{31}P\{^1H\}$ NMR ([D_8]THF, −100 °C): δ −10 to −16.5 (m), −16.5 to −21 (m), −51.8 [s, *cyclo*-(P_4Mes_4)], −53.6 (s), −92 to −100 (m), −102 to −111 (m), −111 to −118 (m), −125 to −127 (m).

Data Collection and Structure Determination of K·1 and Kthf·1. The data were collected on a Siemens SMART CCD diffractometer (λ(Mo Kα) = 0.71073 Å, T = 213(2) K). Semiempirical absorption corrections were carried out with SADABS (Sheldrick, G. M. *SADABS*, *A Program for Empirical Absorption Correction*; Universität of Göttingen: Göttingen, Germany, 1998), and the structures solved with direct methods (Sheldrick, G. M. *SHELXS-97, Program for Crystal Structure Solution*; Universität Göttingen: Göttingen, Germany, 1997). Structure refinement was carried out with SHELXL-97 (Sheldrick, G. M. *SHELXL-97, Program for the Refinement of Crystal Structures*; Universität Göttingen: Göttingen, Germany, 1997).

The crystal of Kthf·**1** was twinned and the structure could also be solved in the monoclinic crystal system in the space groups *C*2 and *C*2/c. Refinement in $P\bar{1}$, using the TWIN and BASF instructions lead to a better refinement (twin matrix = 0 1 0 1 0 0 0 0 1). The structure contains 0.5 molecules of THF as molecule of solvation in the asymmetric unit. All THF molecules in the structure are heavily disordered. The two THF molecules bound to potassium were refined over split positions with constrained geometry and fixed atomic displacement parameters (SAME and EADP instructions). The thermal displacement parameters of these molecules were refined isotropically. All other K, P, O, and C atoms were refined anisotropically.

Table 1. Structural Data of Kthf·**1** and K·**1**

	Kthf·**1**	K·**1**
empirical formula	$C_{58}H_{89}O_{8.5}P_4K$	$C_{62}H_{85}O_6P_4K$
M	1085.33	1089.28
T (K)	213(2)	213(2)
cryst syst	triclinic	monoclinic
space group	$P\bar{1}$	$P2_1/n$
a (Å)	12.188(5)	12.1750(2)
b (Å)	12.371(5)	19.779(2)
c (Å)	22.770(5)	25.449(2)
α (deg)	78.081(5)	90
β (deg)	78.385(5)	97.665(2)
γ (deg)	74.698(5)	90
V (Å^3)	3201(2)	6074(2)
Z	2	4
ρ_{calcd} (Mg m^{-3})	1.164	1.191
θ_{max} (deg)	26.00	23.27
total data	28 920	19 111
unique data (R_{int})	7547	7494 (0.0527)
params (restraints)	780 (53)	659 (120)
GOF on F^2	1.026	1.033
R1, wR2 [$I > 2\sigma(I)$]	0.0784, 0.1960	0.0777, 0.1960
R1, wR2 (all data)	0.1282, 0.2273	0.1166, 0.2174
largest diff. peak and hole (e Å^{-3})	0.669 and −0.448	0.378 and −0.344

The structure of K·**1** contains two very disordered toluene molecules. These were refined over split positions with partial occupancies and restrained atomic distances (DFIX, FLAT instructions). The carbon atoms of these molecules were refined isotropically and three of the carbon atoms were refined with fixed atomic displacement parameters. All other K, P, O, and C atoms were refined anisotropically. The hydrogen atom bound to phosphorus was located on the difference map and refined freely; all other hydrogen atoms were refined on idealized positions. For structural data of Kthf·**1** and K·**1** see Table 1.

Theoretical Calculations. DFT optimizations as well as the calculations of the coupling constants[14] were carried out with the B3LYP functional,[15] the 6-311G(d,p) basis set for P and the relevant H atoms, and the 3-21G basis set for the Mes substituents.[16] Structure **B** (C_1 symmetry): d(P1−P2)/d(P3−P4) = 2.246/2.182 Å, d(P2−P3) = 2.354 Å, d(H−P1) = 1.427 Å, d(H−P4) = 2.811 Å; torsion angles P1−P2−P3−P4 and H−P1−P2−P3 = −24.2 and 14.6°, respectively; $^1J_{P1P2} = -306.1$ Hz, $^1J_{P3P4} = -503.1$ Hz,

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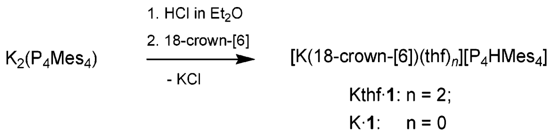
Scheme 1



$^1J_{P2P3} = -279.2$ Hz, $^1J_{HP1} = 180.9$ Hz, $^1J_{HP4} = -5.6$ Hz. Structure **A** (C_2 symmetry): d(P1−P2) = d(P3−P4) = 2.208 Å, d(P2−P3) = 2.339 Å, d(H−P1) = d(H−P4) = 1.778 Å; torsion angles P1−P2−P3−P4 and H−P1−P2−P3 = −20.8 and 14.4°, respectively; $^1J_{P1P2} = {}^1J_{P3P4} = -387.9$ Hz, $^1J_{P2P3} = -232.0$ Hz, $^1J_{HP1} = {}^1J_{HP4} = 13.4$ Hz.

Results and Discussion

Both [K(18-crown[6])(thf)$_2$][P$_4$HMes$_4$] (Kthf·**1**) and its THF-free analogue [K(18-crown-[6])(P$_4$HMes$_4$)] (K·**1**) were obtained as intensely red, crystalline solids by reaction of K$_2$(P$_4$Mes$_4$) with 1 equiv of HCl (dissolved in Et$_2$O) and subsequent addition of 18-crown[6] (Scheme 1). While Kthf·**1** was obtained by recrystallization of the raw material of this reaction in THF, the K·**1** was isolated by recrystallization of the crude product from toluene (see Experimental Section). Single-crystal X-ray structural investigations on Kthf·**1** and K·**1** reveal that the former displays an ion-separated structure in which the potassium cation is coordinated by two THF molecules and a crown ether ligand, while the latter is an ion-contact complex in which the potassium cation is surrounded by one molecule of 18-crown[6] and one terminal phosphorus atom of the P$_4$ chain of **1**.

Table 2. Selected Bond Lengths (Å) and Angles (deg) of Kthf·**1** and K·**1**

Kthf·**1**		K·**1**	
P1−P2	2.198(2)	P1−P2	2.152(2)
P2−P3	2.285(2)	P2−P3	2.276(2)
P3−P4	2.169(2)	P3−P4	2.202(4)
C11−P1	1.850(3)	P1−C101	1.861(6)
C21−P2	1.861(3)	P2 −C201	1.858(5)
C31−P3	1.866(3)	P3−C301	1.855(5)
C41−P4	1.850(3)	P4−C401	1.833(6)
P1−P2−P3	110.55(5)	P1−P2−P3	115.29(8)
P4−P3−P2	111.18(5)	P4−P3−P2	110.68(8)
C11−P1−P2	102.5(1)	C101−P1−P2	99.8(2)
C21−P2−P1	99.7(1)	C201−P2−P1	103.7(2)
C21−P2−P3	101.7(1)	C201−P2−P3	96.5(2)
C31−P3−P4	101.9(1)	C301−P3−P4	101.3(2)
C31−P3−P2	98.7(1)	C301−P3−P2	99.3(2)
C41−P4−P3	103.4(1)	C401−P4−P3	101.7(2)
P1−P2−P3−P4	−13.1	P1−P2−P3−P4	−15.0
		K1−P1	3.364(2)
		P2−P1−K1	117.67(7)
		P4−H1P	1.29(5)
		P3−P4−H1P	99(2)

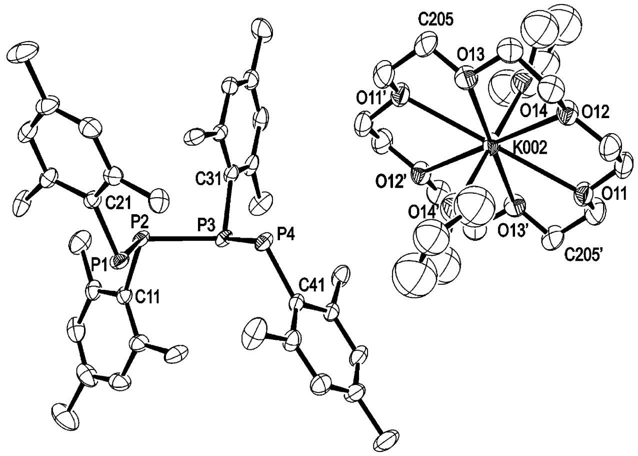


Figure 1. Solid-state molecular structure of [K(18-crown[6])(thf)$_2$]-[P$_4$HMes$_4$] (Kthf·**1**). Only one of the two crystallographically independent [K(18-crown[6])(thf)$_2$]$^+$ units are shown. H atoms and a THF solvent molecule have been omitted for clarity. Thermal ellipsoid level = 30%.

Analysis of the structure of Kthf·**1** was complicated by the fact that the crystals were systematically twinned. The structure was solved in the triclinic space group $P\bar{1}$ (see Experimental Section). The unit cell displays very similar *a* and *b* axes, and the interconversion of the two axes leads to the twinning. Nevertheless, the structure could be refined successfully by using the appropriate twin law. An ion-separated arrangement (Figure 1) is observed in which the two crystallographically independent potassium cations each reside on an inversion center. They are surrounded by an η^6-bound crown ether ligand and two THF molecules. The interactions between the cations and the ligands are in the expected ranges [d(K001−O1, K001−O2, K001−O3, K001−O4) = 2.626(7)−2.808(3) Å, d(K002−O11, K002−O12, K002−O13, K002−O14) = 2.565(8)−2.803(3) Å].[17] Surprisingly, the anion (P$_4$HMes$_4$)$^-$ (**1**) adopts a syn conformation (torsion angle P1−P2−P3−P4 = −13.1°). This is in contrast to the structures of the related doubly protonated tetraphosphane (R^*,S^*,R^*,S^*)-P$_4$H$_2$Mes$_4$ (**2**)[18] and of the related ion-separated tetraphosphanediide salts [M(crypt)]$_2$-[P$_4$R$_4$] (R = Cy, Ph; crypt = 2,2,2-cryptand),[5c] which show strictly anti-periplanar conformations. The P−P bond lengths are in the range for single bonds [d(P1−P2) = 2.198(2) Å, d(P2−P3) = 2.285(2) Å, d(P3−P4) = 2.169(2) Å].[19] Unfortunately, the exact position of the phosphidic proton in **1** could not be ascertained with confidence. However, it is noteworthy that the anion is nearly C_2 symmetric, although it is not situated on a crystallographic symmetry axis [e.g., d(P1−C11) = d(P4−C41) = 1.850(3) Å, d(P2−C21) = 1.861(3) Å, and d(P3−C31) = 1.866(3) Å; C11−P1−P2 = 102.5(1)° and C41−P4−P3 = 103.4(1)°; C21−P2−P1 = 99.2(2)° and C31−P3−P4 = 101.9(1)°, see Table 2]. This may indicate that the proton is located in a symmetric position between the two terminal phosphorus atoms (structure **A**, Scheme 2). However, an alternative explanation may be the disorder of the anion, in which case the observed bond lengths and angles would correspond to average values or a dynamic process in which the proton rapidly exchanges its position between the two terminal phosphorus atoms (structure **B**, Scheme 2). To our knowledge, an intramolecular hydrogen bond between two phosphorus atoms has hitherto

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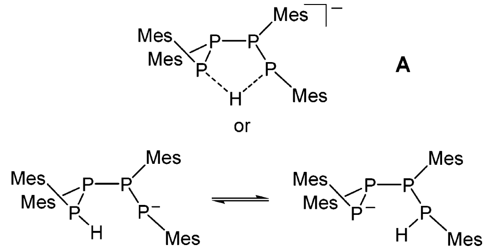
(17) A search in the CCDC database (November 2003 release) gave 21 fragments with a similar structural motif showing K−O contacts from 2.546 to 2.912 Å.

(18) **2** can be synthesized in a manner similar to K·**1** by reaction of K$_2$(P$_4$Mes$_4$) with 2 equiv of HCl in Et$_2$O.[3c] Like the other tetraphosphanes P$_4$H$_2$R$_4$,[5] it decomposes in solution to form a complex mixture of products. Details of the X-ray crystal structure analysis of **2** are given in the Supporting Information.

(19) Blom, R.; Haaland, A. *J. Mol. Struct.* **1985**, *128*, 21.

Scheme 2. Alternative Structures for (P_4HMes_4)$^-$ (**1**)



not been observed. For example, the cation [1,8-(PH_3)(PH_2)-$C_{10}H_6$]$^+$ has an unsymmetrical structure and shows no proton exchange in the solid state or in solution,[20] in contrast to its nitrogen analogue [1,8-(NMe_2H)(NMe_2)$C_{10}H_6$]$^+$, which has been described as a "proton sponge".[21]

Information concerning the position of the proton can be provided by theoretical structure optimization of (P_4HMes_4)$^-$ (**1**) (for details see Experimental Section). From state-of-the-art DFT calculations, it follows that an unsymmetrical syn conformation (structure **B**) is the most stable. The resulting structural parameters match the experimental ones fairly well. For the position of the proton, the following parameters were obtained: d(H−P1) = 1.427 Å, d(H−P4) = 2.811 Å, and torsion angle H−P1−P2−P3 = 14.6°. The alternative symmetric structure **A** (C_2 symmetry, d(H−P1/P4) = 1.778 Å, torsion angle H−P1−P2−P3 = 14.4°) lies 28.3 kJ mol^{-1} higher in energy and represents a first-order saddle point with a decay vibration that moves the proton toward one of the terminal phosphorus atoms. This indicates that structure **A** is the transition state between the two **B** structures.

For comparison, we optimized the anti-periplanar conformation of **1** as well. This structure, with d(H−P1) = 1.412 Å, is 18.0 kJ mol^{-1} less stable than the unsymmetrical syn conformation **B**. Obviously, the latter is stabilized by a certain interaction of the proton with the P4 atom, indicated by some weakening of the H−P1 bond.

The solid-state molecular structure of [K(18-crown[6])-(P_4HMes_4)] (K·**1**) reveals a distinctly different picture from that of Kthf·**1** (Figure 2, Table 2). Again the P_4 chain is in a syn arrangement (torsion angle P1−P2−P3−P4 = −15.0°), but it is clearly asymmetrical, with one of the terminal phosphorus atoms (P1) interacting with the potassium cation [d(K1−P1) = 3.364(2) Å]. The cation is additionally solvated by an η^6-coordinating 18-crown[6] molecule [d(K1−O) = 2.770(7)−2.971(7) Å].[17] The P−P bond lengths follow the expected trend: the shortest bond is formed by the anionic phosphorus atom P1, while the longest P−P bond is observed between the internal phosphorus atoms P2 and P3 [d(P1−P2) = 2.152(2) Å, d(P2−P3) = 2.276(2) Å, d(P3−P4) = 2.220(2) Å]. Significantly, the position of the proton attached to the phosphorus atom could be located from the Fourier difference map and refined freely [d(P4−H1P) = 1.29(5) Å]. This clearly indicates that the proton is bound to the second terminal phosphorus atom P4 to give a trigonal-pyramidal coordination around this atom (sum of angles around P4 = 299.3°). As predicted by the theoretical structure optimization of the free (P_4HMes_4)$^-$ anion (**1**) the proton points inward toward the other terminal phosphorus atom P1 (torsion angle H1P−P4−P3−P2 = −21.2°). However, intramolecular proton transfer, as indicated in Scheme 2, is precluded in this case as the second terminal P atom (P1) is already bound to K1.

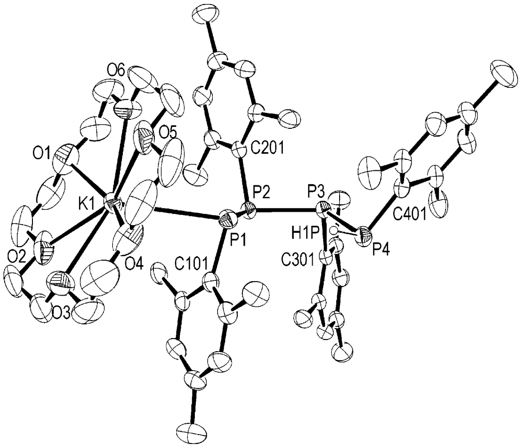


Figure 2. Solid-state molecular structure of [K(18-crown[6])(P_4HMes_4)] (K·**1**). H atoms and toluene solvent molecules have been omitted for clarity (except H1). Thermal ellipsoid level = 30%.

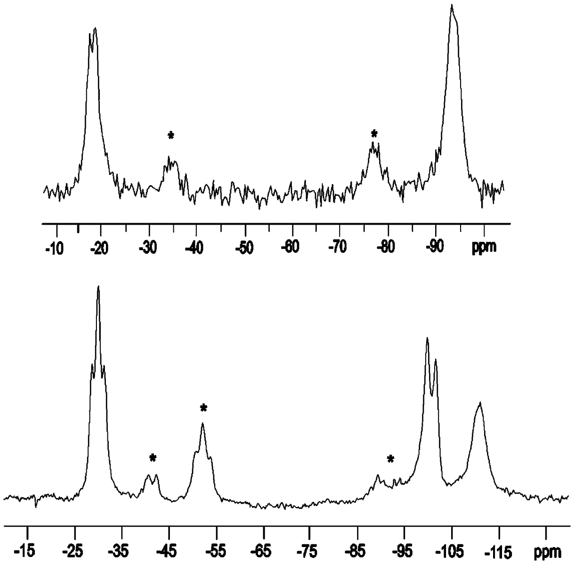


Figure 3. ^{31}P MAS spectra of Kthf·**1** (upper spectrum) and K·**1** (lower spectrum) at 202.45 MHz (* denotes spinning sidebands).

The asymmetry of the anion K·**1** is reflected in its solid-state ^{31}P MAS NMR spectrum (Figure 3). An intense low-field signal at −30.0 ppm can be assigned to the internal phosphorus atoms, which are isochronous, while two less-intense resonances at −100.7 and −110.8 ppm can be assigned to the terminal phosphorus atoms of the P_4 chain, which have different chemical environments. In contrast, the solid-state ^{31}P MAS NMR spectrum of Kthf·**1** supports a symmetric structure of the anion with two broad multiplets at −17.9 and −93.3 ppm of approximately equal intensity (Figure 3).

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(21) Reiter, S.; Nogai, D.; Karaghiosoff, K.; Schmidbaur, H. *J. Am. Chem. Soc.* **2004**, *126*, 15833.

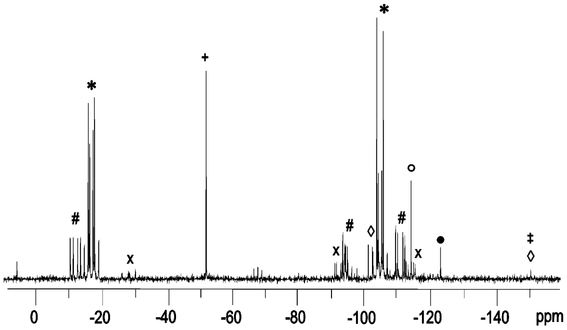

Figure 4. $^{31}P\{^{1}H\}$ NMR spectrum of Kthf·**1** in [D$_8$]THF at −100 °C (161.98 MHz) (# = (R^*,S^*)-$(P_3HMes_3)^-$, × = (R^*,R^*)-$(P_3HMes_3)^-$, * = **1**, + = *cyclo*-(P_4Mes_4), ○ = (R^*,R^*)-$P_2H_2Mes_2$, ● = (R,S)-$P_2H_2Mes_2$, ◇ = *cyclo*-(P_3Mes_3), ‡ = PH_2Mes).

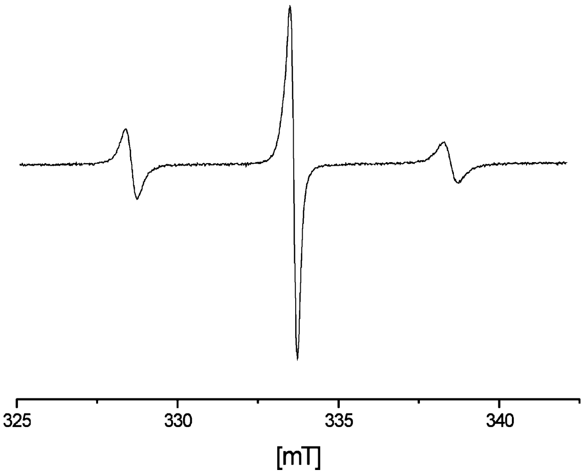

Figure 5. X-band EPR spectrum of a solution of Kthf·**1** in THF at room temperature ($F \approx 9.5$ GHz, $g_0 = 2.014979$, $a_0 = 5.0$ mT = 141.01 MHz).

In solution, the very broad peaks observed in the room-temperature ^{31}P NMR spectra of crystalline Kthf·**1** and K·**1** in C_6D_6, C_7D_8, and THF indicate a fluxional process. The signals remain broad in C_7D_8 even at −80 °C, while the ^{31}P NMR spectra of THF solutions at −100 °C display well-resolved multiplets (Figure 4). These can be assigned to $(P_4HMes_4)^-$ (**1**) (AA′BB′X spin system, 59% referred to the total P content), (R^*,R^*)-$(P_3HMes_3)^-$ (ABCX spin system, ∼21%), (R^*,S^*)-$(P_3HMes_3)^-$ (ABCX spin system, ∼4%; for details of the assignment, see Supporting Information), (R^*,R^*)-$P_2H_2Mes_2$ (∼5%), (R^*,S^*)-$P_2H_2Mes_2$ (∼3%),[8h] *cyclo*-(P_4Mes_4) (∼6%),[22] *cyclo*-(P_3Mes_3) (∼1%),[22] and PH_2Mes (∼1%).[23] Furthermore, concentrated THF solutions of Kthf·**1** show an intense triplet in the X-band EPR spectrum, corresponding to the presence of the $(P_2Mes_2)^-$ radical anion as a further component in solution (Figure 5).[24] The observation of a complex mixture of products in solution shows that **1** undergoes redistribution reactions leading to an equilibrium between several distinct neutral and anionic species in solution. In contrast, **1** appears to be indefinitely stable at room temperature in the solid state with exclusion of air and moisture and may be obtained in pure form from solution by crystallization.

The observation of a symmetric AA′BB′X spin system for **1** in the low-temperature $^{31}P\{^{1}H\}$ NMR spectrum may lead to ambiguous conclusions concerning its structure. Notably, the P−P coupling constants in **1** are in the expected range, while the ^{1}J(P−H) coupling constant of the terminal phosphorus atoms P_B and $P_B{}'$ shows a value of only ±108.8 Hz, which is approximately half the magnitude generally observed in other phosphanes and alkali metal phosphanides. A decreased magnitude of ^{1}J(P−H) is expected for a symmetric position of the proton between the two terminal phosphorus atoms (structure **A**, Scheme 2). This hypothesis is also supported by the calculated coupling constants (see Experimental Section). At first glance, an asymmetrical structure, such as **B** (Scheme 2), appears to be ruled out, since this would result in an ABCDX spin system. However, rapid proton transfer may lead to an averaging of this spin system to give an AA′BB′X spin system with a reduced magnitude of the ^{1}J(P−H) coupling constant as well. Thus, neither structural possibility can be discarded on the basis of the NMR spectroscopic measurements alone.

Further information on the structure of **1** was expected from vibrational spectroscopy. Primary and secondary phosphanes and phosphanides usually show P−H vibrations in the region of 2300−2400 cm^{-1}, in both the IR and Raman spectra. A significant downshift of the P−H stretching frequency should be observed for the hydrogen-bridged structure **A** (Scheme 2) but not for the asymmetrical structure **B**. However, no signal was detected in the characteristic P−H region in the IR spectra (in Nujol) or in the Raman spectra of solid Kthf·**1** and K·**1** (see Supporting Information). In the case of Kthf·**1**, this supports the presence of hydrogen-bridged structure **A** as the vibration analysis of the optimized structure **B** yields an IR- and Raman-active vibration at 2295 cm^{-1} (or 1649 cm^{-1} for the deuterated compound). In contrast, the ion-contact complex K·**1** shows an asymmetrical structure of the anion according to its X-ray crystal structure and the solid-state ^{31}P NMR spectrum (vide infra). Therefore, a P−H vibration in the normal range would be expected for this compound. To exclude the possibility of a shift of the P−H vibration resulting from the presence of hydrogen bonding (which would be very unlikely for K·**1**), we prepared the deuterated analogue [K(18-crown-[6])(thf)$_2$][P_4DMes_4] (Kthf·**3**). Both Kthf·**3** and Kthf·**1** show very similar spectroscopic and analytical data (see Supporting Information). In particular, the IR and Raman spectra of both compounds are virtually identical. Thus, there is no significant isotopic shift of any vibration.

Conclusions

In this paper, we have presented a detailed study of the synthesis and the remarkable structural properties of the tetraphosphanide anion $(P_4HMes_4)^-$ (**1**). In solution, **1** forms an equilibrium with several other oligophosphane and oligophosphanide species, while in the solid state, this anion can be isolated in pure form as the potassium salts K·**1** and Kthf·**1**. The structural puzzle associated with **1** illustrates

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[22] Frenzel, C.; Hey-Hawkins, E. *Phosphorus, Sulfur, Silicon Relat. Elem.* **1998**, *143*, 1.

[23] Oshikawa, T.; Yamashita, M. *Chem. Ind. (London)* **1985**, 126.

[24] The formation of such radical anions has already been observed upon addition of cryptands to solutions of alkali metal oligophosphanediides $M_2(P_nR_n)$.[3b,4c]

that, even with the advanced analytical and theoretical methods available today, it may still be extremely challenging to determine the structure of a rather simple inorganic compound. Most likely, **1** displays an asymmetrical structure in which the proton is exclusively bound to one of the terminal P atoms (as is in fact observed in the solid-state structure of K·**1**). However, the observation of a symmetric spin system in the ^{31}P NMR spectrum of **1** in solution and the rather symmetric solid-state structure of the THF adduct Kthf·**1** seem to indicate that, under certain conditions, the proton is able to fluctuate between the two terminal phosphorus atoms of the P_4 chain.

In future work, it remains to be seen whether the structures of other tetraorganotetraphosphanides are analogous to that of **1**. Preliminary investigations reveal that the closely related sodium salt [Na(18-crown[6])(thf)$_2$][P_4HMes_4] has a very similar structure to Kthf·**1**.[25] In fact, it appears likely that the lability observed for **1** in solution is a general feature of such anions that would severely restrict their synthetic utility. Moreover, this observation seems to imply that traces of protons may act as a catalyst for the transformation of linear oligophosphanediide anions, which may explain why reactions involving such species frequently take a serendipitous course.[4c,5b,26−28]

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Supporting Information Available: Raman and IR spectra of [K(18-crown[6])(thf)$_2$][P_4HMes_4] (Kthf·**1**), [K(18-crown[6])-(P_4HMes_4)] (K·**1**), and [K(18-crown[6])(thf)$_2$][P_4DMes_4] (Kthf·**3**), further details of the NMR spectroscopic characterisation of Kthf·**1** and K·**1**, and details of the X-ray crystal structure analysis of (R^*,S^*,R^*,S^*)-$P_4H_2Mes_4$ (**2**). This material is available free of charge via the Internet at http://pubs.acs.org. CCDC 293599 (Kthf·**1**), 602799 (K·**1**), and 293600 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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(26) Köpf, H.; Voigtländer, R. *Chem. Ber.* **1981**, *114*, 2731.
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