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# Nucleophilic Degradation of White Phosphorus with *t*Bu$_3$SiK: Synthesis and X-ray Crystal Structure Analysis of the Potassium Triphosphide (*t*Bu$_3$Si)$_2$P$_3$K

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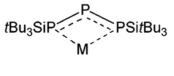
*Summary: The potassium phosphides (tBu$_3$Si)$_2$P$_4$K$_2$ and (tBu$_3$Si)$_4$P$_8$K$_4$ can be synthesized from the reaction of P$_4$ with 2 equiv of the potassium silanide tBu$_3$SiK in tetrahydrofuran at −78 °C. The potassium silanide tBu$_3$SiK slowly transforms the tetraphospide (tBu$_3$Si)$_2$P$_4$K$_2$ and the octaphosphide (tBu$_3$Si)$_4$P$_8$K$_4$ into (tBu$_3$Si)$_2$P$_3$K and (tBu$_3$Si)$_3$P$_5$K$_2$. X-ray quality crystals of the triphosphide, tBu$_3$SiKP−P=PSitBu$_3$, have been obtained from a tetrahydrofuran solution at −25 °C.*

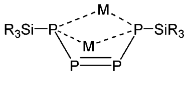
## Introduction

Recently we have reported on the reaction of P$_4$ with the silanides *t*Bu$_3$SiM (M = Li, Na) and *t*Bu$_2$PhSiNa in a 1:3 stoichiometry, which cleanly led to the tetraphosphides (*t*Bu$_3$Si)$_3$P$_4$M$_3$ (M = Li, Na) and (*t*Bu$_2$PhSi)$_3$P$_4$Na$_3$. However, the solid state structure of tetraphosphide (*t*Bu$_3$Si)$_3$P$_4$Li$_3$ features a dimer. This tetraphosphide can be transformed into the unsaturated triphosphide (*t*Bu$_3$Si)$_2$P$_3$Li and the monophosphide *t*Bu$_3$SiPLi$_2$.[1]

Otherwise, the reaction of P$_4$ with *t*Bu$_3$SiM (M = Li, Na) and *t*Bu$_2$PhSiNa in a molar ratio of 1:2 leads to the sodium tetraphosphides **2**, (*t*Bu$_3$Si)$_2$P$_4$M$_2$ (M = Li, Na), and (*t*Bu$_2$PhSi)$_2$P$_4$Na$_2$, which dimerize in weakly polar solvents to the octaphosphides (*t*Bu$_3$Si)$_4$P$_8$M$_4$ (M = Li, Na) and (*t*Bu$_2$PhSi)$_4$P$_8$Na$_4$.[2]



**1**



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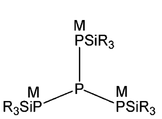

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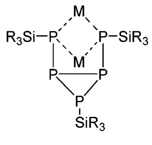
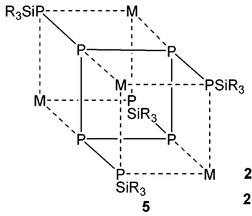


**4**



**5**

**2a-5a**: R$_3$Si = *t*Bu$_3$Si, M=Li, Na, K
**2b-5b**: R$_3$Si =*t*Bu$_2$PhSi, M=Na

In this paper, we describe the reaction of P$_4$ with the silanide *t*Bu$_3$SiK[3] in a 1:3 and 1:2 stoichiometry, respectively. When *t*Bu$_3$SiK is employed as a reaction partner of P$_4$, some novel insight into the nucleophilic degradation of white phosphorus can be expected. In contrast to the well-established Zintl-type alkali phosphides P$_n$M$_x$, only a limited number of molecular alkali phosphides R$_m$P$_n$M$_x$ have been structurally characterized by X-ray crystallography.

## Results and Discussion

We expected that the analogous potassium tetraphosphide (*t*Bu$_3$Si)$_3$P$_4$K$_3$ will be produced when P$_4$ is reacted with 3 equiv of *t*Bu$_3$SiK. By contrast, when P$_4$ was treated with 3 equiv of *t*Bu$_3$SiK in tetrahydrofuran, first the tetraphosphide (*t*Bu$_3$Si)$_2$P$_4$K$_2$ and the octaphosphide (*t*Bu$_3$Si)$_4$P$_8$K$_4$ were formed as main products, rather than the tetraphosphide (*t*Bu$_3$Si)$_3$P$_4$K$_3$.

Surprisingly, after the reaction mixture had been stored at ambient temperature for three weeks, the resonances of (*t*Bu$_3$Si)$_2$P$_4$K$_2$ and (*t*Bu$_3$Si)$_4$P$_8$K$_4$ were no longer observable in the $^{31}$P NMR spectrum and signals had grown, which can be assigned to the pentaphosphide (*t*Bu$_3$Si)$_3$P$_5$K$_3$ (34% of P atoms), the triphosphide (*t*Bu$_3$Si)$_2$P$_3$K (42% of P atoms), and the monophosphide *t*Bu$_3$SiPK$_2$ (24% of P atoms). Apparently, the unreacted potassium silanide *t*Bu$_3$SiK has slowly transformed the tetraphosphide (*t*Bu$_3$Si)$_2$P$_4$K$_2$ and the octaphosphide (*t*Bu$_3$Si)$_4$P$_8$K$_4$ into the triphosphide (*t*Bu$_3$Si)$_2$P$_3$K and the pentaphosphide(*t*Bu$_3$Si)$_3$P$_5$K$_2$.

As shown in Scheme 1, the silanide *t*Bu$_3$SiK causes the decomposition of the tetraphosphide (*t*Bu$_3$Si)$_2$P$_4$K$_2$ and the octaphosphide (*t*Bu$_3$Si)$_4$P$_8$K$_4$; *t*Bu$_3$SiPK$_2$ is formed.[4] Contrary to the lithium tetraphosphide (*t*Bu$_3$Si)$_3$P$_4$Li$_3$, the related potassium tetraphosphide (*t*Bu$_3$Si)$_3$P$_4$K$_3$ is as yet unknown. The triphosphide (*t*Bu$_3$Si)$_2$P$_3$K may be produced via an intermediary tetraphosphide (*t*Bu$_3$Si)$_3$P$_4$K$_3$.

On the other hand, the tetraphosphide (*t*Bu$_3$Si)$_2$P$_4$K$_2$ and the octaphosphide (*t*Bu$_3$Si)$_4$P$_8$K$_4$ were formed in high yield by the addition of 2 equiv of *t*Bu$_3$SiK to 1 equiv of P$_4$ in tetrahydrofuran. Orange crystals of the

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[1] Lerner, H.-W.; Wagner, M.; Bolte, M. *J. Chem. Soc., Chem. Commun.* **2003**, 990.

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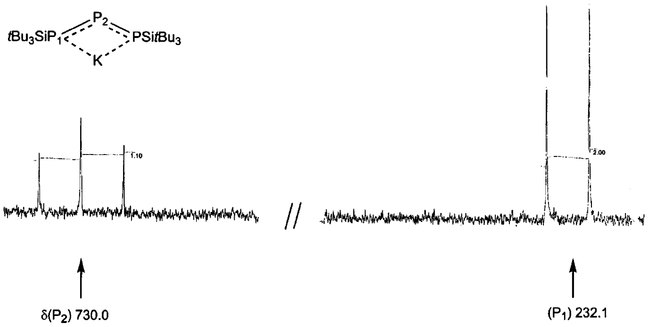
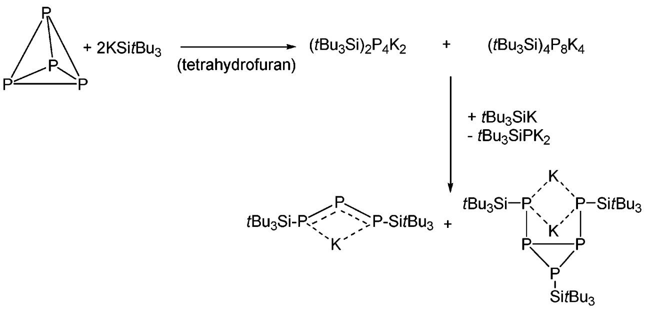


**Figure 1.** Observed $^{31}P\{^1H\}$ NMR spectrum of **1a(K)** in $d_8$-THF at 109.37 MHz (25 °C; external $H_3PO_4$): $\delta$ 730.0 (t, $^1J_{P1P2}$ = 552.34 Hz; $P_2$); 232.1 (d, $^1J_{P1P2}$ = 552.34 Hz; $P_1$).

**Scheme 1**



octaphosphide $(tBu_3Si)_4P_8K_4$ were grown from the reaction solution at ambient temperature.[8] Unfortunately, the tetraphosphide $(tBu_3Si)_2P_4K_2$ has yet to be isolated. However, its structure can be proven unambiguously from its $^{31}P$ NMR spectrum.

Generally, the NMR spectra of potassium phosphides **1a(K)**–**5a(K)** resemble those of the lithium and sodium phosphides **1a(Li,Na)**–**5(Li,Na)**.[1,2,5,6] The $^{31}P\{^1H\}$NMR spectrum of the triphosphide **1(K)** features two signals with the splitting pattern of an $AX_2$ spin system in the range for the unsaturated two-coordinate phosphorus atoms, as shown in Figure 1. The $^{31}P\{^1H\}$ NMR spectrum of the potassium tetraphoshide **2a(K)** shows multiplets with the splitting pattern of an AA′XX′ spin system (Figure 2) similar to the spectra of the tetraphosphides **2a(Na)** and **2b(Na)**. The $^{31}P\{^1H\}$ NMR spectra of the potassium octaphophide **5a(K)** and the sodium phosphides **5a(Na)** and **5b(Na)**[2] exhibit the same general features. As indicated in Figure 3, the $^{31}P\{^1H\}$ NMR spectrum of the pentaphosphide **4a(K)** shows three multiplets with the splitting pattern of an AA′BB′MM′ spin system. The $^{31}P$ NMR data of phosphorus compounds **1**–**5** are listed in Table 1.

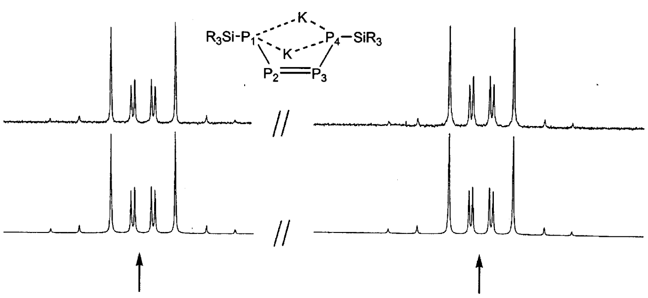


**Figure 2.** Observed and calculated $^{31}P\{^1H\}$ NMR spectrum of **2a(K)** in $d_8$-THF at 109.37 MHz (25 °C; external $H_3PO_4$): $\delta$ 408.3 (m, $^1J_{P2P3} = -386.20$ Hz, $^1J_{P1P2} = {}^1J_{P3P4} = -448.83$ Hz, $^2J_{P1P3} = {}^2J_{P2P4} = 33.87$ Hz; $P_2$, $P_3$); $-5.1$ (m, $^3J_{P1P4} = 121.15$ Hz, $^1J_{P1P2} = {}^1J_{P3P4} = -448.83$ Hz, $^2J_{P1P3} = {}^2J_{P2P4} = -33.87$ Hz; $P_1$, $P_4$).

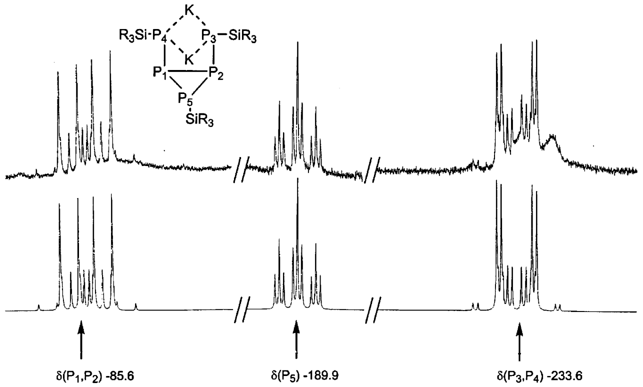


**Figure 3.** Observed and calculated $^{31}P\{^1H\}$ NMR spectrum of **4a(K)** in $d_8$-THF at 109.37 MHz (25 °C; external $H_3PO_4$): $\delta$ $-85.6$ (m, $^1J_{P1P2} = -168.80$ Hz, $^1J_{P1P3} = {}^1J_{P2P4} = -363.80$ Hz, $^2J_{P1P4} = {}^2J_{P2P3} = 7.59$ Hz, $^1J_{P1P5} = {}^1J_{P2P5} = -202.44$ Hz; $P_1$, $P_2$), $-189.9$ (m, $^2J_{P3P5} = {}^2J_{P4P5} = 48.72$ Hz, $^1J_{P1P5} = {}^1J_{P2P5} = -202.44$ Hz; $P_5$), $-233.6$ (m, $^1J_{P1P3} = {}^1J_{P2P4} = -363.80$ Hz, $^1J_{P1P5} = {}^1J_{P2P5} = -202.44$ Hz, $^3J_{P3P4} = 187.37$ Hz, $^2J_{P1P4} = {}^2J_{P2P3} = 7.59$ Hz, $^2J_{P3P5} = {}^2J_{P4P5} = 48.72$ Hz; $P_3$, $P_4$).

**Table 1. $^{31}$P NMR Data for Alkali Metal Phosphides of the Type 1, 2, 3, 4, and 5**

| | M = Na | M = K | M = Na |
|---|---|---|---|
| | $R_3Si = tBu_3Si$ | $R_3Si = tBu_3Si$ | $R_3Si = tBu_2PhSi$ |
| **1** | $\delta$($d_8$-THF) 732.5, 212.5 | $\delta$($d_8$-THF) 730.0, 232.1 | *a* |
| **2** | $\delta$($d_8$-THF) 403.0, −41.1 | $\delta$($d_8$-THF) 408.3, −5.1 | $\delta$($d_8$-THF) 396.1, −41.7 |
| **3** | $\delta$($C_6D_6$) −11.0, −100.0 | *a* | $\delta$($C_6D_6$) −31.5, −108.5 |
| **4** | $\delta$($C_6D_6$) −93.4, −179.6, −240.3 | $\delta$($d_8$-THF) −85.6, −189.9, −233.6 | $\delta$($d_8$-THF) −90.0, −181.5, −243.1 |
| **5** | $\delta$($C_6D_6$) 25.2, −176.8 | $\delta$($d_8$-THF) 12.0, −180.0 | $\delta$($d_8$-THF) 21.5, −185.6 |

[a] Unknown.

The crystal structure of triphosphide **[1a(K)(THF)$_2$]$_2$** is shown in Figure 4; selected bond lengths and angles can be found in the corresponding caption. X-ray quality crystals of **[1a(K)(THF)$_2$]$_2$** (monoclinic, *C*2/*c*) were grown from tetrahydrofuran. It is interesting to note that $(tBu_3Si)_2P_3K$ represents the second structurally characterized triphosphaallyl alkali metal compound, but the quality of its crystal structure is much better than that of the sodium triphosphide $(tBu_3Si)_2P_3Na$.[5] A similar structural motif has been observed for a few complexes of transition metals.[7]

The molecular structure of the triphosphide **[1a(K)(THF)$_2$]$_2$** shows two short PP bonds and an almost

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(8) **5a(K)**: cell dimensions $a = 13.5188$ Å, $b = 13.4814$ Å, $c = 25.4352$ Å, $\alpha = 99.461°$, $\beta = 100.264°$, $\gamma = 100.264°$, $V = 4207$ Å$^3$, $T = 173(2)$ K. The structure determination failed.

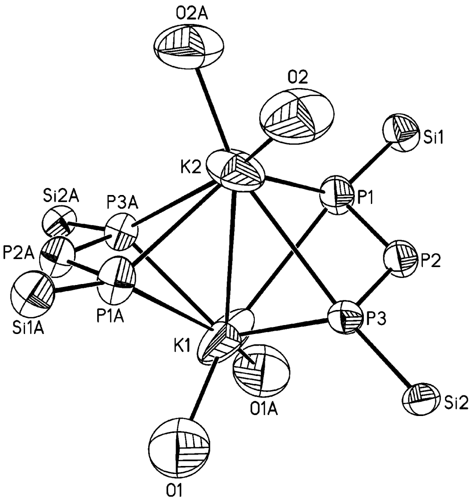

**Figure 4.** Thermal ellipsoid plot of **[1a(K)(THF)$_2$]$_2$** showing the atomic numbering scheme. The displacement ellipsoids are drawn at the 50% probability level. *t*Bu groups have been omitted for clarity. Selected bond lengths [Å] and angles [deg]: P−Si 2.2700(12) [av], Si−C 1.952(5) [av], P−P−P 101.05(6) [av], Si−P−P 117.29(6) [av], C−Si−C 110.60(20) [av].

**Table 2. Crystal Data and Structure Refinement for [1a(K)(THF)$_2$]$_2$**

| | |
|---|---|
| empirical formula | $C_{64}H_{140}K_2P_6O_4Si_4$ |
| color | purple |
| shape | plate |
| fw | 1350.14 |
| cryst syst | monoclinic |
| space group | *C*2/*c* |
| *a*, Å | 15.6637(12) |
| *b*, Å | 22.0460(16) |
| *c*, Å | 25.0214(18) Å |
| α, deg | 90 |
| *β*, deg | 106.071(6) |
| *γ*, deg | 90 |
| volume, Å$^3$ | 8302.8(11) |
| *Z* | 4 |
| density(calcd), Mg/m$^3$ | 1.080 |
| abs coeff *μ*(Mo Kα), mm$^{-1}$ | 0.325 |
| *F*(000) | 2960 |
| cryst size, mm$^3$ | 0.36 × 0.32 × 0.23 |
| diffractometer | Stoe-IPDS-II |
| *θ*-range, deg | 2.51 to 25.43 |
| index ranges | $-18 \le h \le 18$,<br>$-26 \le k \le 26$,<br>$-29 \le l \le 29$ |
| no. of reflns collected | 29 752 |
| no. of indep reflns | 7339 |
| *R*(int) | 0.0555 |
| absorp corr | empirical, MULABS |
| $T_{\min}$, $T_{\max}$ | 0.8919, 0.9289 |
| no. of data/restraints/params | 7339/5/362 |
| goodness of fit on $F^2$ | 0.918 |
| final *R* indices [$I > 2\sigma(I)$], R1, wR2 | 0.0694, 0.1861 |
| peak/hole, eÅ$^{-3}$ | 0.856 and −0.327 |

planar W-shaped SiPPPSi skeleton with a P−P distance of 2.0721(16) Å. This distance is in the range of PP double bonds and shorter than the sum of the atomic radii (sum of the atomic radii: 2.20 Å). As depicted in Figure 5, the two silyl-substituted triphosphaallylic anions are bridged by two K cations to form a dimer in the solid state. The triphosphide **[1a(K)(THF)$_2$]$_2$** features four P−K contacts (P−K distance: 3.4757(16) Å, average) for every K atom. Apart from these P atoms, the K atoms are coordinated by two tetrahydrofuran molecules.

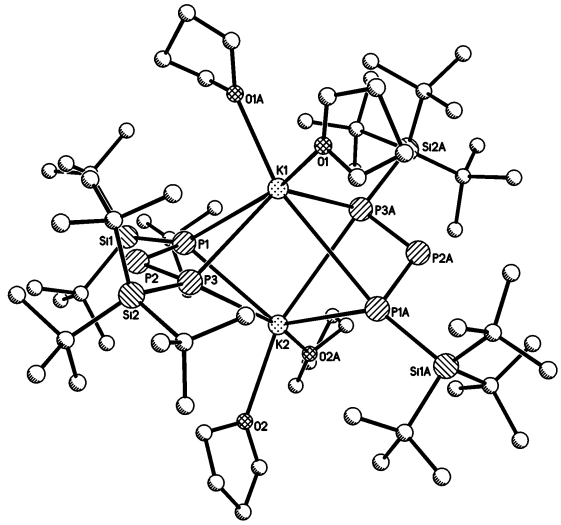

**Figure 5.** Molecular structure of **[1a(K)(THF)$_2$]$_2$**.

## Experimental Section

**General Procedures.** All experiments were carried out under dry argon with strict exclusion of air and moisture using standard Schlenk techniques. *t*Bu$_3$SiK[3] was prepared according to literature procedures. The solvents (benzene, toluene, tetrahydrofuran) were distilled from sodium/benzophenone prior to use.

The NMR spectra were recorded on a JEOL GSX 270, a JEOL EX, a Bruker AM 250, a Bruker DPX 250, and a Bruker Avance 400 spectrometer. The $^{29}$Si NMR spectra were recorded using the INEPT pulse sequence with empirically optimized parameters for polarization transfer from the *t*Bu substituents. Abbrevations: s = singlet; d = doublet; t = triplet; q = quartet; mult = multiplet; br = broad; m = meta; o = ortho; p = para.

**Reaction of P$_4$ with 3 equiv of *t*Bu$_3$SiK.** *t*Bu$_3$SiK (0.806 g, 3.39 mmol) in tetrahydrofuran (20 mL) was added to freshly sublimed P$_4$ (0.141 g, 1.14 mmol) at ambient temperature and stirred for 2 h. According to the $^{31}$P NMR spectrum, the tetraphosphide (*t*Bu$_3$Si)$_2$P$_4$K$_2$ and the octaphosphide (*t*Bu$_3$Si)$_4$P$_8$K$_4$ were formed as the main products. After the reaction mixture had been stored at ambient temperature for three weeks, the resonances of (*t*Bu$_3$Si)$_2$P$_4$K$_2$ (47% of P atoms) and (*t*Bu$_3$Si)$_4$P$_8$K$_4$ (52% of P atoms) were no longer observable in the $^{31}$P NMR spectrum and signals had grown, which can be assigned to the compounds (*t*Bu$_3$Si)$_3$P$_5$K$_3$ (34% of P atoms), (*t*Bu$_3$Si)$_2$P$_3$K (42% of P atoms), and *t*Bu$_3$SiPK$_2$[4] (24% of P atoms). X-ray quality crystals of **1a(K)(THF)$_2$** were obtained after the reaction mixture had been concentrated in vacuo to a volume of 5 mL and kept at −25 °C for 1 month. Yield: 0.209 g (17%). Selected data for (*t*Bu$_3$Si)$_2$P$_3$K, **1(K)**: $^1$H NMR ($d_8$-THF, internal TMS): *δ* 1.08 (br, 54H; *t*Bu). $^{13}$C{$^1$H} NMR ($d_8$-THF, internal TMS): *δ* 24.0 (br; *C*Me$_3$), 31.8 (br; C*Me$_3$*). $_{31}$P{$^1$H} NMR (see Figure 1 and Table 1). $^{29}$Si{$^1$H} NMR ($d_8$-THF, external TMS): *δ* 17.1 (m; Si*t*Bu$_3$). Selected data for (*t*Bu$_3$Si)$_3$P$_5$K$_2$, **4a(K)**: $^1$H NMR (C$_6$D$_6$, internal TMS): *δ* 1.30 (br, 54H *t*Bu), 1.22 (br, 27H; *t*Bu). $^{13}$C{$^1$H} NMR (C$_6$D$_6$, internal TMS): *δ* 25.4 (s; *C*Me$_3$), 25.5 (s; *C*Me$_3$), 32.4 (s; C*Me$_3$*), 32.8 (s; C*Me$_3$*). $^{31}$P{$^1$H} NMR (see Figure 3 and Table 1). $^{29}$Si{$^1$H} NMR ($d_8$-THF, external TMS): *δ* 30.6 (dt; 2 Si*t*Bu$_3$), 17.4 (m; Si*t*Bu$_3$). Selected data for *t*Bu$_3$SiPK$_2$: $^1$H NMR ($d_8$-THF, internal TMS): *δ* 1.06 (br, 27H; *t*Bu). $^{31}$P{$^1$H} NMR ($d_8$-THF, external H$_3$PO$_4$): *δ* −320.4 (br).

**Reaction of P$_4$ with 2 equiv of *t*Bu$_3$SiK.** *t*Bu$_3$SiK (0.629 g, 2.64 mmol) in tetrahydrofuran (20 mL) was added to a solution of freshly sublimed P$_4$ (0.146 g, 1.18 mmol) in 10 mL of tetrahydrofuran at −78 °C and stirred for 2 h. According to the $^{31}$P NMR spectrum, the tetraphosphide (*t*Bu$_3$Si)$_2$P$_4$K$_2$ (40% of P atoms) and the octaphosphide (*t*Bu$_3$Si)$_4$P$_8$K$_4$ (50% of P atoms) were formed as the main products. Orange crystals[8] of $(t\mathrm{Bu}_3\mathrm{Si})_4\mathrm{P}_8\mathrm{K}_4$, **5a(K)**, were obtained after the reaction mixture had been stored at ambient temperature for 1 week (yield: 0.175 g 21%).

Selected data for $(t\mathrm{Bu}_3\mathrm{Si})_2\mathrm{P}_4\mathrm{K}_2$, **2a(K)**: $^1$H NMR ($d_8$-THF, internal TMS): $\delta$ 1.07 (br, 54H; *t*Bu). $^{13}$C{$^1$H} NMR ($d_8$-THF, internal TMS): $\delta$ 25.3 (s; *C*Me$_3$), 32.8 (s; C*Me*$_3$). $^{29}$Si{$^1$H} NMR ($d_8$-THF, external TMS): $\delta$ 21.4 (m; Si*t*Bu$_3$). $^{31}$P{$^1$H} NMR (see Figure 2 and Table 1). Selected data for $(t\mathrm{Bu}_3\mathrm{Si})_4\mathrm{P}_8\mathrm{K}_4$, **5a(K)**: $^1$H NMR ($d_8$-THF, internal TMS): $\delta$ 1.09 (br, 108H; *t*Bu). $^{13}$C{$^1$H} NMR ($d_8$-THF, internal TMS): $\delta$ 26.3 (s; *C*Me$_3$), 32.4 (s; C*Me*$_3$). $^{29}$Si{$^1$H} NMR ($d_8$-THF, external TMS): $\delta$ 19.8 (m; Si*t*Bu$_3$). $^{31}$P{$^1$H} NMR (see Table 1).

**X-ray Structure Determination.** Data collection: Stoe-IPDS-II diffractometer, graphite-monochromated Mo Kα radiation; $T = 173$ K, empirical absorption correction using MULABS,[9] structure solution by direct methods,[10] structure refinement: full-matrix least-squares on $F^2$ with SHELXL-97.[11] Hydrogen atoms were placed on ideal positions and refined with fixed isotropic displacement parameters using a riding model. CCDC reference number: 211011.

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**Supporting Information Available:** The table of X-ray parameters, atomic coordinates and thermal parameters, and bond distances and angles. This material is available free of charge via the Internet at http://pubs.acs.org.

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