

# A Convenient Synthetic Strategy toward Heavy Alkali Metal Bis(trimethylsilyl)phosphides: Crystal Structures of the Ladder-Type Polymers $[A(\text{thf})\text{P}(\text{SiMe}_3)_2]_\infty$ ( $A = \text{K}, \text{Rb}, \text{Cs}$ )

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A series of highly reactive heavy alkali metal phosphides was prepared by treating trimethylsilyl-substituted phosphines with alkali metal *tert*-butyl alcoholates. The compounds are formed in excellent yield and purity, and the side product can be easily removed in a vacuum. The high synthetic potential of this reaction route was further shown by utilizing excess alkali metal *tert*-butyl alcoholates in reaction with silyl substituted phosphines. In all cases, only monometalated products were isolated. In the course of this work the crystal structures of the bis(trimethylsilyl)phosphides  $[\text{K}(\text{thf})\text{P}(\text{SiMe}_3)_2]_\infty$ , **1a**,  $[\text{Rb}(\text{thf})\text{P}(\text{SiMe}_3)_2]_\infty$ , **1b**, and  $[\text{Cs}(\text{thf})\text{P}(\text{SiMe}_3)_2]_\infty$ , **1c**, were obtained. The compounds display polymeric ladder-type structures. Compounds **1a,b** are isomorphous, while compound **1c** displays a slightly altered local geometry. Despite small differences in local geometry, the coordination spheres for the phosphorus atoms and the alkali metal are fairly similar. The five coordinate phosphorus atoms are connected to three alkali metal centers in addition to two trimethylsilyl groups. The alkali metals are four coordinate with ligations to three phosphorus centers in addition to one thf oxygen donor. Compounds **1a–c** were characterized using elemental analysis, NMR spectroscopy, and X-ray crystallography. Crystal data with Mo K $\alpha$  ( $\lambda = 0.71073 \text{ \AA}$ ) at 150 K are as follows: **1a**,  $a = 6.4261(2) \text{ \AA}$ ,  $b = 12.4119(2) \text{ \AA}$ ,  $c = 21.5447(4) \text{ \AA}$ ,  $V = 1718.41(7) \text{ \AA}^3$ ,  $Z = 4$ , orthorhombic, space group  $P2_12_12_1$ , 3427 independent reflections,  $R1$  (all data) = 0.0351; **1b**,  $a = 6.5338(2) \text{ \AA}$ ,  $b = 12.5664(3) \text{ \AA}$ ,  $c = 21.5537(5) \text{ \AA}$ ,  $V = 1769.70(8) \text{ \AA}^3$ ,  $Z = 4$ , orthorhombic, space group  $P2_12_12_1$ , 4195 independent reflections,  $R1$  (all data) = 0.0776; **1c**,  $a = 11.3515(1) \text{ \AA}$ ,  $b = 22.3445(3) \text{ \AA}$ ,  $c = 7.2501(1) \text{ \AA}$ ,  $\beta = 96.017(1)^\circ$ ,  $V = 1828.81(4) \text{ \AA}^3$ ,  $Z = 4$ , monoclinic, space group  $P2_1/c$ , 4343 independent reflections,  $R1$  (all data) = 0.0811.

## Introduction

Lithium bis(trimethylsilyl)phosphide, initially described by Fritz and Hölderlich,<sup>1</sup> has found widespread interest as reagent in organic synthetic chemistry<sup>2</sup> and as important bis(trimethylsilyl)phosphide transfer reagent in both main group and transition metal chemistry.<sup>3</sup> This synthetic utility resulted in considerable interest in the structural chemistry of lithium bis(trimethylsilyl)phosphides. Of specific interest was the influence of the donor on the association and aggregation properties and the question on how this would influence the reactivity of the target compounds. These investigations resulted in the synthesis and solid-state analysis of about a handful of donor-containing and donor-free lithium bis(trimethylsilyl)phosphides, such as

the dimeric  $[\text{Li}(\text{thf})_2\text{P}(\text{SiMe}_3)_2]_2$ <sup>4</sup> and  $[\text{Li}(\text{DME})\text{P}(\text{SiMe}_3)_2]_2$ ,<sup>5</sup> exhibiting central, planar  $\text{Li}_2\text{P}_2$  four-membered rings with four coordinate lithium and phosphorus centers. Utilization of the tridentate donor PMDTA (=N,N,N',N'',N''-pentamethyldiethylenetriamine) resulted in the presumably monomeric  $\text{Li}(\text{PMDTA})\text{P}(\text{SiMe}_3)_2$  (no crystal structure is available).<sup>4</sup> A higher degree of association is observed if the amount of donor is limited, or no donor is utilized, as seen in the tetrameric  $[\text{LiP}(\text{SiMe}_3)_2]_4(\text{thf})_2$ <sup>4</sup> or the hexameric  $[\text{LiP}(\text{SiMe}_3)_2]_6$ .<sup>6</sup> This short list of compounds shows impressively the direct influence of the donor on the association behavior in the lithium phosphides. Despite the different degrees of association very related structural patterns are observed; all structures can be related to a ladder-type motif: the monomer  $\text{Li}(\text{PMDTA})\text{P}(\text{SiMe}_3)_2$  displays one Li–P rung, the dimers  $[\text{Li}(\text{thf})_2\text{P}(\text{SiMe}_3)_2]_2$  and  $[\text{Li}(\text{DME})\text{P}(\text{SiMe}_3)_2]_2$  exhibit two rungs, and the tetramer  $[\text{LiP}(\text{SiMe}_3)_2]_4(\text{thf})_2$  and hexamer  $[\text{LiP}(\text{SiMe}_3)_2]_6$  display four and six Li–P rungs, respectively.

In contrast to the relatively well-studied chemistry of lithium phosphides there is a dearth of information in regards to synthetic strategies and structural chemistry of the heavier alkali

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metal phosphides. The interest in heavier alkali metal target compounds arises from their enhanced reactivity, as compared to the lithium analogues, important for the synthesis of alkaline-earth lanthanide and actinide derivatives and for the formation of phosphorus–phosphorus bonds.<sup>7</sup>

Examples of heavier alkali metal phosphides have been limited to the spectroscopically characterized [APH<sub>2</sub>]<sub>∞</sub>,<sup>8</sup> [AP-Ph<sub>2</sub>]<sub>∞</sub>,<sup>9</sup> and [AP(SiMe<sub>3</sub>)<sub>2</sub>]<sub>∞</sub><sup>10,11</sup> (A = Na, K, Rb, and Cs). Structural reports are available for a small number of sodium phosphides such as the dimeric [NaP-2-OMeC<sub>6</sub>H<sub>4</sub>]<sub>2</sub><sup>12</sup> and [Na-(PMDTA)P(H)(C<sub>6</sub>H<sub>11</sub>)]<sub>2</sub>.<sup>13</sup> Examples of potassium derivatives include the polymeric [KP(H)Mes\*]<sub>∞</sub> (Mes\* = 2,4,6-*t*-Bu<sub>3</sub>C<sub>6</sub>H<sub>2</sub>)<sup>14</sup> and the dimeric [K(thf)<sub>2</sub>P(2,4,6-Me<sub>3</sub>C<sub>6</sub>H<sub>2</sub>)Si(F)-*t*-Bu]<sub>2</sub>.<sup>15</sup> Potassium–phosphorus contacts are also observed in the transition metal phosphides Cp\*<sub>2</sub>ZrP<sub>3</sub>K(thf)<sub>1.5</sub> (Cp\* = C<sub>5</sub>-Me<sub>5</sub>)<sup>16</sup> and Cp<sub>2</sub>ZrHKPMes\*(thf)<sub>2</sub>,<sup>17</sup> the phospholy complex [(Tmp)<sub>6</sub>Sm<sub>2</sub>(KCl)<sub>2</sub>(C<sub>7</sub>H<sub>8</sub>)<sub>3</sub>]<sub>∞</sub> (Tmp = 2,3,4,5-tetramethylphospholy),<sup>18</sup> a series of tetraphospholide derivatives,<sup>19</sup> and a fulvalene analogue [K<sub>2</sub>(*μ*-DME)<sub>2</sub>tetraphenyldiphosphafulvalene]<sub>∞</sub>.<sup>20</sup> The cesium phosphide [Cs(py)<sub>2</sub>P(H)Mes\*]<sub>n</sub> has been mentioned in the literature, but detailed structural data are not available.<sup>21</sup>

A common synthetic strategy toward sodium and potassium phosphides involves the treatment of primary or secondary phosphines with alkali metal hydrides. While this method works well for the sodium and potassium phosphides, the corresponding rubidium and cesium derivatives are inaccessible due to lack of easily available, soluble alkali metal hydrides. A previously published synthetic paper concerned with rubidium and cesium phosphides relied on the treatment of primary or secondary phosphines with elemental rubidium or cesium under addition of naphthalene.<sup>10</sup> Since naphthalene is a solid with excellent crystallization properties, contamination of the reaction products was frequently observed. Moreover, the synthesis of primary or secondary phosphines is required, often a time-consuming process, made more difficult by the high reactivity of small primary and secondary phosphines which ignite spontaneously upon contact with air.

Recent work from Uhlig et al., published as a preliminary communication,<sup>11</sup> focused on the development of an alternative synthetic strategy, involving the treatment of the less reactive tertiary trimethylsilyl-substituted phosphines with alkali *tert*-butyl alcoholates. This reaction scheme produced reliably lithium, sodium, and potassium phosphides with concurrent formation of the silyl ether. This work has now been extended toward the heavier, more reactive alkali metal analogues. We are further exploring the synthetic potential of this reaction route by utilizing excess of alkali metal reagents to investigate the possibility of di- and trimetalation of the phosphine precursors.

Our interest in heavy alkali metal phosphide chemistry also extends toward the investigation of their solid-state properties to obtain insight into how differently sized alkali metals will influence the structural parameters of the target compounds. In the course of this work we have structurally characterized the highly reactive heavy alkali metal silylphosphides [K(thf)P-(SiMe<sub>3</sub>)<sub>2</sub>]<sub>∞</sub>, **1a**, [Rb(thf)P(SiMe<sub>3</sub>)<sub>2</sub>]<sub>∞</sub>, **1b**, and [Cs(thf)P(SiMe<sub>3</sub>)<sub>2</sub>]<sub>∞</sub>, **1c**.

## Experimental Section

**General Procedures.** All reactions were performed under purified nitrogen atmosphere by using either modified Schlenk techniques or a Braun Labmaster 100 drybox. *n*-Hexane, toluene (tol), and tetrahydrofuran (thf) were freshly distilled from a Na/K alloy and degassed two times before use. Commercially available KO-*t*-Bu, was used as received. P(SiMe<sub>3</sub>)<sub>3</sub>,<sup>10</sup> RbO-*t*-Bu,<sup>22</sup> CsO-*t*-Bu,<sup>22</sup> and PhP(SiMe<sub>3</sub>)<sub>2</sub><sup>23</sup> were synthesized according to literature procedures. <sup>1</sup>H (400.13 MHz) and <sup>13</sup>C NMR (100.63 MHz) spectra were obtained utilizing a DPX400 spectrometer (Bruker). <sup>31</sup>P (121.49 MHz) and <sup>29</sup>Si (59.63 MHz) NMR spectra are measured with a DRX300 (Bruker) spectrometer.

**General Synthetic Procedure for Compounds 1a–c.** The compounds were prepared similar to the method developed by Uhlig et al., as described in an earlier communication.<sup>11</sup> In a typical experiment 5 mmol of P(SiMe<sub>3</sub>)<sub>3</sub> (1.25 g) were treated with an equimolar amount of potassium, rubidium, or cesium *tert*-butyl alcoholate in 30 mL of thf at room temperature. The mixtures were stirred for 4 h at ambient temperature, resulting in slightly turbid colorless solutions. The volatiles were removed in a vacuum, resulting in white powders. The powders were extracted at room temperature using a small amount of toluene (typically 10 mL). The extracts were filtered through Celite-padded filter frits, and the resulting solutions were placed in a freezer at –20 °C. After a short time, white amorphous precipitates formed which were isolated by filtration. The powders were left in a vacuum for several hours. Depending on the extent of the vacuum treatment, products with varying degree of thf were isolated: the donor-free products [AP(SiMe<sub>3</sub>)<sub>2</sub>]<sub>∞</sub> became available after extended treatment (>6 h) as confirmed by elemental analyses and NMR spectroscopy. X-ray-quality crystals were grown by dissolving the donor-free powders in a small amount of thf which was then layered with *n*-hexane and stored at 5 °C for several days. The X-ray crystal structure analyses indicated that under those conditions the mono-thf adducts were formed. Exposure of compounds **1a–c** to vacuum resulted in the formation of alkali metal phosphides with a reduced ratio of thf:metal. NMR spectroscopic data for the various alkali phosphides are summarized in Table 1.

[K(thf)P(SiMe<sub>3</sub>)<sub>2</sub>]<sub>∞</sub>, **1a**. A 1.25 g (5 mmol) amount of P(SiMe<sub>3</sub>)<sub>3</sub> and 0.56 g (5 mmol) of KO-*t*-Bu were combined in 20 mL of thf. After removal of the volatiles, toluene extraction, and extended exposure to vacuum, the powder was identified as [KP(SiMe<sub>3</sub>)<sub>2</sub>]<sub>∞</sub> (0.81 g 75%). Mp: 350 °C (dec). Anal. Found (calc): K, 17.6 (18.01). After recrystallization from a thf/hexane mixture, X-ray-quality crystals of [K(thf)P(SiMe<sub>3</sub>)<sub>2</sub>]<sub>∞</sub>, **1a**, were isolated in quantitative yield. Mp: 65–68 °C. Anal. Found (calc): K, 12.7 (13.54).

[Rb(thf)P(SiMe<sub>3</sub>)<sub>2</sub>]<sub>∞</sub>, **1b**. A 1.25 g (5 mmol) amount of P(SiMe<sub>3</sub>)<sub>3</sub> and 0.79 g (5 mmol) of RbO-*t*-Bu were combined in 20 mL of thf.

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**Table 1.**  $^{31}\text{P}$ ,  $^1\text{H}$ , and  $^{29}\text{Si}$  Spectral NMR Data for Compounds 1–3

	formula	$^{31}\text{P}$ NMR ( $\delta$ in ppm)	$^{29}\text{Si}$ NMR [ $\delta$ in ppm ( $^1J_{\text{Si-P}}$ in Hz)]	$^1\text{H}$ NMR [ $\delta_{\text{SiMe}_3}$ in ppm ( $^3J_{\text{P-H}}$ in Hz)]	$^1\text{H}$ NMR ( $\delta$ for solvent in ppm)
<b>3'</b>	KPh $_2$ <sup>a</sup>	−14.0			
<b>2a</b>	NaP(Ph)SiMe $_3$ <sup>a</sup>	−156.3			
<b>3b</b>	KP(Ph)SiMe $_3$ <sup>a</sup>	−148.0	0.6 (52 ± 3) <sup>b</sup>	0.07 (18 H, 3.5)	
<b>1a</b>	[K(thf)P(SiMe $_3$ ) $_2$ ] $_{\infty}$	−293.4	0.7 (54 ± 3) <sup>b</sup>	0.085 (18 H, 3.35)	1.72 (6 H, CH $_2$ ); 3.69 (6–7 H, OCH $_2$ )
<b>1b</b>	[Rb(thf)P(SiMe $_3$ ) $_2$ ] $_{\infty}$	−287.1	0.41 (55 ± 3) <sup>b</sup>	0.04 (18 H, 3.1)	1.70 (7 H, CH $_2$ ); 3.75 (6–7 H, OCH $_2$ )
<b>1c</b>	[Cs(thf)P(SiMe $_3$ ) $_2$ ] $_{\infty}$	−270.0	0.5 (52 ± 3) <sup>b</sup>	0.065 (18 H, 3.5)	1.73 (7 H, CH $_2$ ); 3.70 (7–8 H, OCH $_2$ )
<b>1d'</b>	NaP(SiMe $_3$ ) $_2$ ·2thf	−304.3	0.6 (50 ± 5) <sup>b</sup>	0.01 (18 H, 3.4)	1.75 (8 H, CH $_2$ ); 3.66 (8 H, OCH $_2$ )

<sup>a</sup> Determined via NMR spectroscopy. <sup>b</sup> Broad signals. <sup>c</sup> In thf.

After removal of the volatiles, toluene extraction, and extended exposure to vacuum, the powder was identified as [RbP(SiMe $_3$ ) $_2$ ] $_{\infty}$  (1.05 g, 80%). After recrystallization from a thf/hexane mixture 1.1 g (65%) of [Rb(thf)P(SiMe $_3$ ) $_2$ ] $_{\infty}$ , **1b**, was isolated. Mp: 69–73 °C. Anal. Found (calc): Rb, 24.4 (25.52).

[Cs(thf)P(SiMe $_3$ ) $_2$ ] $_{\infty}$ , **1c**. A 1.25 g (5 mmol) amount of P(SiMe $_3$ ) $_3$  and 1.02 g (5 mmol) of CsO-*t*-Bu were combined in 20 mL of thf. After removal of the volatiles, toluene extraction, and extended exposure to vacuum, the powder was identified as [CsP(SiMe $_3$ ) $_2$ ] $_{\infty}$  (1.2 g, 75%). After recrystallization from a thf/hexane mixture 1.52 g (80%) of [Cs(thf)P(SiMe $_3$ ) $_2$ ] $_{\infty}$ , **1c**, was isolated. Mp: 65–70 °C. Anal. Found (calc): Cs, 36.1 (34.76).

**Treatment of P(SiMe $_3$ ) $_3$  with Excess KO-*t*-Bu.** A 1.25 g (5 mmol) amount of P(SiMe $_3$ ) $_3$  was dissolved in 50 mL of thf and treated with a 3-fold excess of KO-*t*-Bu (1.73 g, 15.5 mmol). The reaction mixture was refluxed for 4 h, after which the amount of solvent was reduced to 10 mL. The resulting solution was analyzed by utilizing  $^{31}\text{P}$  NMR spectroscopy.  $^{31}\text{P}$  NMR (ppm): −293.5.

**Treatment of PhP(SiMe $_3$ ) $_2$  with Excess KO-*t*-Bu.** A 1.01 g (4 mmol) amount of PhP(SiMe $_3$ ) $_2$  was dissolved in 50 mL of thf and treated with a double excess of KO-*t*-Bu (0.9 g (8 mmol)). The reaction mixture was refluxed for 4 h, after which the amount of solvent was reduced to 10 mL. The resulting solution was analyzed by using  $^{31}\text{P}$  NMR spectroscopy.  $^{31}\text{P}$  NMR (ppm): −148.0.

**Treatment of PhP(SiMe $_3$ ) $_2$  with Excess NaO-*t*-Bu.** A 1.52 g (6 mmol) amount of PhP(SiMe $_3$ ) $_2$  was dissolved in 50 mL of thf and treated with 1.15 g (12 mmol) of NaO-*t*-Bu. The reaction mixture was refluxed for 12 h, after which the amount of solvent was reduced to 10 mL. The remaining solution was analyzed by utilizing  $^{31}\text{P}$  NMR spectroscopy.  $^{31}\text{P}$  NMR (ppm): −156.3.

**X-ray Crystallographic Studies.** X-ray-quality crystals for all compounds were grown as described in the Experimental Section. The crystals were removed from the Schlenk tube under a stream of N $_2$  and immediately placed in a highly viscous hydrocarbon oil (Paratone N, Exxon). A suitable crystal was selected under the microscope, attached to a glass fiber, and immediately placed in the low-temperature nitrogen stream of the diffractometer.<sup>24</sup> Typically, the samples decomposed within 30 s or less; **1c** ignited upon contact with air. Data sets for all compounds were collected using a Siemens SMART system complete with 3-circle goniometer and CCD detector operating at −54 °C. The data collection nominally covered a hemisphere of reciprocal space, by a combination of three sets of exposures; each set had a different  $\phi$  angle, and each exposure covered 0.3° in  $\omega$ . The data sets of all compounds were collected at −123 °C using a Cryojel low-temperature device from Oxford Instruments. For all compounds graphite-monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) was employed. Crystal decay was monitored by repeating a set of initial frames at the end of the data collection and analyzing the duplicate reflections. No decay was observed. An absorption correction was applied by utilizing the program SADABS.<sup>25</sup> Extinction effects were disregarded. The crystal structures of all compounds were solved by direct methods as included in the SHELXTL program package.<sup>26</sup>

Missing atoms were located in subsequent difference Fourier maps and included in the refinement. The structures of all compounds were refined by full-matrix least-squares refinement on  $F^2$  (SHELX-93).<sup>27</sup> Hydrogen atoms were placed geometrically and refined using a riding model, including free rotation about C–C bonds for methyl groups. For all compounds, hydrogen atoms were refined with  $U_{\text{iso}}$  constrained at 1.2 for nonmethyl groups and 1.5 for methyl groups times  $U_{\text{eq}}$  of the carrier C atom. The crystallographic programs used for structure refinement and solution were installed either on a PC clone or a Silicon Graphics Indigo2 R10000 Solid Impact. Scattering factors were those provided with the SHELX program system.<sup>27</sup> All non-hydrogen atoms were refined anisotropically. Some of the carbon atoms in the thf donor molecules show larger positional parameters. An attempt to refine some of the disordered positions by utilizing split positions and modeling the disorder did not result in an improved model. The atoms are therefore included with single positions. Table 2 summarizes important data in regards to data collection, structure solution, and refinement. Table 3 presents selected geometrical data. Further details about the data collections, structure solutions, and refinements and how disorder was handled are outlined in the Supporting Information.

## Results and Discussion

**Syntheses.** The highly reactive potassium, rubidium, and cesium bis(trimethylsilyl)phosphides were prepared in good yield and purity by treatment of tris(trimethylsilyl)phosphine with 1 molar equiv of the respective alkali metal *tert*-butyl alcoholate. The products were typically obtained as colorless highly air-sensitive, pyrophoric powders, isolated after initial extraction with toluene. The powders were dried in vacuum for several hours to yield quantitatively the donor-free product [AP(SiMe $_3$ ) $_2$ ] $_{\infty}$  (A = K, Rb, Cs). The purity of the reaction products was confirmed by bulk analysis. The powders can be transformed into X-ray-quality crystals by dissolving the amorphous powders in very small amounts of thf (<5 mL) followed by careful layering with *n*-hexane. After filtration, the solutions were stored at 5 °C for several days during which the crystals were formed. The crystalline solids were identified as the mono-thf derivatives [A(thf)P(SiMe $_3$ ) $_2$ ] $_{\infty}$  (A = K, Rb, Cs), **1a–c**, utilizing X-ray crystallography.

Several synthetic procedures toward alkali metal silylphosphides have been mentioned in the literature. One of the most effective ones involves the treatment of trimethylsilyl-substituted phosphines with alkali metal *tert*-butanolates (eq 1), as described in an preliminary communication for the lighter alkali metal analogues, lithium, sodium, and potassium.<sup>11</sup>



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**Table 2.** Summary of Data Collection, Structure Solution, and Refinement of Compounds **1a–c**

	compd		
	<b>1a</b>	<b>1b</b>	<b>1c</b>
formula	C <sub>10</sub> H <sub>26</sub> KOPSi <sub>2</sub>	C <sub>10</sub> H <sub>26</sub> OPRbSi <sub>2</sub>	C <sub>10</sub> H <sub>26</sub> OPCsSi <sub>2</sub>
fw	288.56	334.93	382.37
cryst shape	colorless needle	colorless needle	colorless needle
cryst size (mm)	0.8 × 0.1 × 0.1	0.6 × 0.08 × 0.08	0.06 × 0.06 × 0.09
<i>a</i> (Å)	6.4261(2)	6.5338(2)	11.3515(1)
<i>b</i> (Å)	12.4119(2)	12.5664(3)	22.3445(3)
<i>c</i> (Å)	21.5447(4)	21.5537(5)	7.2501(1)
α (deg)	90	90	90
β (deg)	90	90	96.017(1)
γ (deg)	90	90	90
<i>V</i> (Å <sup>3</sup> )	1718.41(7)	1769.70(8)	1828.81(4)
<i>Z</i>	4	4	4
space group	<i>P</i> 2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>	<i>P</i> 2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>	<i>P</i> 2 <sub>1</sub> / <i>c</i>
<i>d</i> <sub>calc</sub> (g/cm <sup>3</sup> )	1.115	1.257	1.389
lin abs coeff (cm <sup>-1</sup> )	5.22	30.05	22.25
radiation	Mo Kα	Mo Kα	Mo Kα
<i>T</i> (°C)	-123	-123	-123
2θ range (deg)	4–57	4–57	4–57
indep refl ( <i>R</i> <sub>int</sub> )	3427 (0.0406)	4195 (0.0615)	4343 (0.0610)
no. params	136	137	136
<i>R</i> 1, <i>wR</i> 2 (all data) <sup>a</sup>	0.0351, 0.0676	0.0776, 0.131	0.0811, 0.1083
<i>R</i> 1, <i>wR</i> 2 (>2σ) <sup>a</sup>	0.0302, 0.0660	0.0554, 0.122	0.0481, 0.0973

$$^a R1 = \sum ||F_o| - |F_c|| / \sum |F_o|, wR2 = \sqrt{\sum w \{(F_o)^2 - (F_c)^2\}^2 / \sum w \{(F_o)^2\}^2}.$$

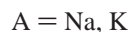
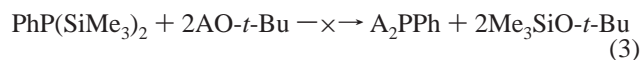
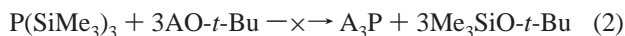
**Table 3.** Important Bond Lengths (Å) and Angles (deg) in [K(thf)P(SiMe<sub>3</sub>)<sub>2</sub>]<sub>∞</sub>, **1a**, [Rb(thf)P(SiMe<sub>3</sub>)<sub>2</sub>]<sub>∞</sub>, **1b**, and [Cs(thf)P(SiMe<sub>3</sub>)<sub>2</sub>]<sub>∞</sub>, **1c**

compd	A–P (Å)	A–donor (Å)	P–Si (Å)	P–A–P (deg)	CN (metal)
<b>1a</b>	3.3169(7), 3.4063(8), 3.4272(8)	2.781(2)	2.110(8), 2.2146(7)	98.79(2), 99.21(2), 140.23(2)	4
<b>1b</b>	3.416(1), 3.484(2), 3.486(2)	2.899(5)	2.208(2), 2.213(2)	98.42(4), 98.46(4), 139.29(5)	4
<b>1c</b>	3.582(1), 3.645(1), 3.667(1)	3.056(4)	2.197(2), 2.198(2)	95.14(3), 95.51(3), 165.11(4)	4

The easy availability of the heavy alkali metal *tert*-butyl alcoholates<sup>23</sup> makes this route ideally suited for the preparation of the heavy alkali metal target molecules. The synthetic versatility of this route is demonstrated by the wide choice of possible phosphine reagents: reaction of tris(trimethylsilyl)phosphines P(SiMe<sub>3</sub>)<sub>3</sub> with alkali metal *tert*-butyl alcoholates results in bis(trimethylsilyl)-substituted derivatives (**1**) and utilization of bis(trimethylsilyl)organo substrates RP(SiMe<sub>3</sub>)<sub>2</sub> yields trimethylsilylorgano phosphides (**2**), while (trimethylsilyl)diorgano-substituted phosphines R<sub>2</sub>P(SiMe<sub>3</sub>) result in the diorgano-substituted phosphides (**3**).

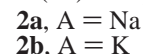
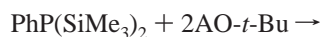
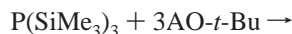


The synthetic potential of this reaction is further underscored by analyzing a series of experiments involving treatment of tris(trimethylsilyl)phosphine (eq 2) or phenylbis(trimethylsilyl)phosphine (eq 3) with excess sodium or potassium *tert*-butanolate.



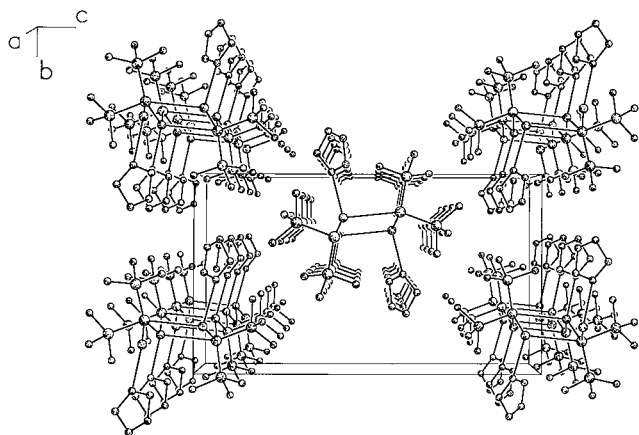
Interestingly, the sole reaction products in reactions 2 and 3 are the monometalated products [K(thf)<sub>*n*</sub>P(SiMe<sub>3</sub>)<sub>2</sub>]<sub>*m*</sub>, [Na(thf)<sub>*n*</sub>P(Ph)SiMe<sub>3</sub>]<sub>*m*</sub>, and [K(thf)<sub>*n*</sub>P(Ph)SiMe<sub>3</sub>]<sub>*m*</sub> (*n* = 0, 1, 2; *m* = 0–∞)

(eqs 4 and 5). This result can be reproduced even after extended reflux in thf.

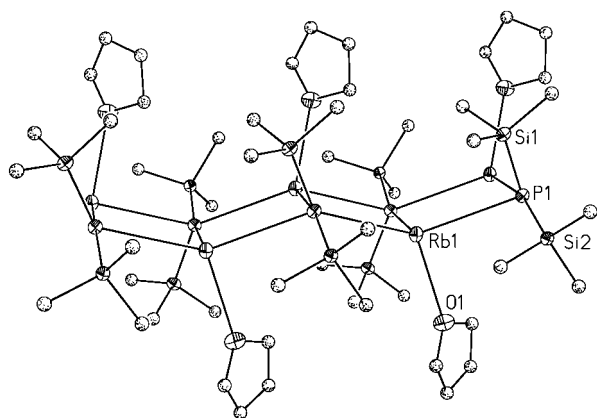


Important to note is that in no instance a further loss of a trimethylsilyl group was observed, an occurrence mentioned in the earlier literature.<sup>1,4</sup> Moreover, no yield-reducing side reactions, even after extended reflux time (>12 h), were observed. The repeated isolation of monometalated products in excellent yields and purity, even when nonstoichiometric reagent amounts were utilized, indicates the high synthetic utility of this synthetic route.

**Structural Descriptions.** [K(thf)P(SiMe<sub>3</sub>)<sub>2</sub>]<sub>∞</sub>, **1a**, and [Rb(thf)P(SiMe<sub>3</sub>)<sub>2</sub>]<sub>∞</sub>, **1b**. Compounds **1a,b** crystallize in an isomorphous fashion, displaying puckered polymeric ladder-type structures. Figure 1 displays an extended view of the unit cell displayed in **1a**, and a part of the ladder-type polymer strand of compound **1b** is shown in Figure 2. Each asymmetric unit contains one alkali metal metal, one thf donor, and one bis(trimethylsilyl)phosphide unit. The ladder polymer is generated by a 2-fold screw axis located in the center of a A<sub>2</sub>P<sub>2</sub> ring. The alkali metals are linked to three phosphorus centers in addition to one thf oxygen atom. The potassium–phosphorus distances range between 3.3169(7) and 3.4272(8) Å; the corresponding



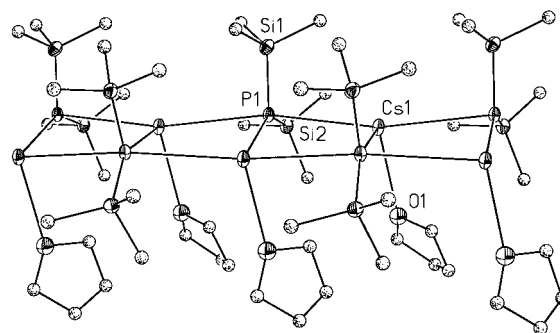
**Figure 1.** Computer-generated plot showing an extended view of the unit cell displayed in **1a**. Hydrogen atoms have been removed for clarity.



**Figure 2.** Computer-generated plot showing part of the ladder-type polymer of compound **1b**. Hydrogen atoms have been omitted for clarity.

rubidium linkages are observed between 3.416(1) and 3.486(2) Å. The alkali metal–oxygen interactions are found at 2.781(2) and 2.899(5) Å. The metal centers display a distorted tetrahedral environment with P–A–P angles ranging between 98.79(2) and 140.23(2)° for **1a** and 98.42(4) and 139.29(5)° for **1b**. Each of the phosphorus atoms is linked to three alkali metal centers, in addition to two silicon contacts from the trimethylsilyl ligands. This results in a severely distorted trigonal bipyramidal coordination at phosphorus with angles ranging between 80.84(2) and 153.11(2)° for **1a** and 81.54(4) and 156.11(8)° for **1b**. The puckered shape of the ladder becomes evident by analysis of the P(1)–alkali metal–P(1)#2 angles (140.23(2), **1a**, and 139.29(5)°, **1b**).

[Cs(thf)P(SiMe<sub>3</sub>)<sub>2</sub>]<sub>n</sub>, **1c**. Compound **1c** crystallizes as a polymeric, ladder-type structure shown in Figure 3. Each asymmetric unit contains one cesium, one thf, and one bis(trimethylsilyl)phosphide ligand. The ladder polymer is generated by a glide plane along *c* axis. The polymeric ladder is formed by the dimerization of rungs containing alternating cesium and phosphorus atoms, resulting in four-membered Cs<sub>2</sub>P<sub>2</sub> rings in which each cesium atom is connected to three phosphorus atoms in addition to thf oxygen ligation. The cesium–phosphorus contacts are observed between 3.582(1) and 3.667(1) Å, and the Cs–O bond length is found at 3.056(4) Å. This arrangement results in a distorted tetrahedral coordination sphere at cesium with P–Cs–P angles ranging between 95.14(3) and 165.11(4)°. The phosphorus atoms are linked to three cesium centers, in addition to two silicon linkages with Cs–Si



**Figure 3.** Computer-generated plot showing a part of the polymeric ladder-type structure of **1c**. Hydrogen atoms have been omitted for clarity.

bond lengths of 2.197(2) and 2.198(2) Å. This results in a distorted trigonal bipyramidal coordination sphere with angles at phosphorus between 84.03(3) and 165.11(4)°. The slight puckering of the ladder is exemplified by the almost linear P(1)–Cs–P(1)#2 angle of 165.11(4)°.

**Structural Chemistry.** The most important structural feature of compounds **1a–c** is their polymeric ladder-type structure. The isomorphous compounds **1a,b** display a large degree of ladder puckering (P(1)–alkali metal–P(1)#2 140.23(2) (1a) and 139.29(5)° (1b)), while **1c** exhibits an almost flat ladder arrangement with a P(1)–Cs–P(1)#2 angle of 165.11(4)°.

The ladder motif is well-known in lithium chemistry,<sup>28</sup> and numerous amides, phosphides, phenolates, thiolates, selenolates, and tellurolates displaying this structural type have been described.<sup>29</sup> In contrast, structural information in regards to the heavier alkali metal congeners is much more limited. Among those, sodium and potassium species have been studied most intensively,<sup>30</sup> while information about the most reactive alkali metal derivatives rubidium and cesium is extremely scarce. Examples of heaviest alkali metal derivatives include a series of alkali metal thiolates, where the large terphenyl ligand S-2,6-R<sub>2</sub>C<sub>6</sub>H<sub>4</sub> (R = 2,4,6-*i*-Pr<sub>3</sub>C<sub>6</sub>H<sub>2</sub>) made possible the formation of dimeric  $\pi$ -arene-stabilized dimers.<sup>31</sup> Other examples include a well-characterized heterocubane [CsN(H)SiMe<sub>3</sub>]<sub>4</sub><sup>32</sup> and the cesium phosphide [Cs(py)<sub>2</sub>P(H)Mes\*]<sub>n</sub>; however, detailed structural information about this compound is not available.<sup>21</sup>

- (28) (a) Gregory, K.; Schleyer, P. V. R.; Snaith, R. *Adv. Inorg. Chem.* **1991**, 37, 47. (b) Pauer, P.; Power, P. P. In *Lithium Chemistry: A Theoretical and Experimental Overview*; Sapse, A. M., Schleyer, P. v. R., Eds.; Wiley: New York, 1995.
- (29) See for example: (a) Jones, R. A.; Stuart, A. L.; Wright, T. C. *J. Am. Chem. Soc.* **1983**, 105, 7459. (b) Aslam, M.; Bartlett, R. A.; Block, E.; Olmstead, M. M.; Power, P. P.; Sigel, G. E. *J. Chem. Soc., Chem. Commun.* **1985**, 1674. (c) Banister, A. J.; Clegg, W.; Gill, W. R. *J. Chem. Soc., Chem. Commun.* **1987**, 850. (d) Barr, D.; Clegg, W.; Mulvey, R. E.; Snaith, R. *J. Chem. Soc., Chem. Commun.* **1989**, 57. (e) Driess, M.; Huttner, G.; Knopf, N. K.; Pritzkow, H.; Zsolnay, L. *Angew. Chem., Int. Ed. Engl.* **1995**, 34, 316. (f) Ruhlandt-Senge, K.; Englich, U.; Senge, M. O.; Chadwick, S. *Inorg. Chem.* **1996**, 35, 5820. (g) Kowach, G. L.; Warren, C. J.; Haushalter, R. C.; DiSalvo, F. J. *Inorg. Chem.* **1998**, 37, 156.
- (30) See for example: (a) Tesh, K. F.; Hanusa, T. P.; Huffman, J. C. *Inorg. Chem.* **1990**, 29, 1584. (b) Brooker, S.; Edelman, F. T.; Kottke, T.; Roesky, H. W.; Sheldrick, G. M.; Stalke, D.; Whitmire, K. H. *J. Chem. Soc., Chem. Commun.* **1991**, 144. (c) Bonasia, P. J.; Arnold, J. J. *Organomet. Chem.* **1993**, 449, 147. (d) Rose, D. J.; Chang, Y. D.; Chen, Q.; Kettler, P. B.; Zubietta, J. *Inorg. Chem.* **1995**, 34, 3973. (e) Hogerheide, M. P.; Ringelberg, S. N.; Janssen, M. D.; Boersma, J.; Spek, A. L.; van Koten, G. *Inorg. Chem.* **1996**, 35, 1195. (f) Ruhlandt-Senge, K.; Englich, U. *Chem. Commun.* **1996**, 147. (g) Chadwick, S.; Englich, U.; Ruhlandt-Senge, K. *Organometallics* **1997**, 16, 5792. (h) Englich, U.; Chadwick, S.; Ruhlandt-Senge, K. *Inorg. Chem.* **1998**, 37, 283.
- (31) Niemeyer, M.; Power, P. P. *Inorg. Chem.* **1996**, 35, 7264.
- (32) Tesh, K. F.; Jones, B. D.; Hanusa, T. P.; Huffman, J. C. *J. Am. Chem. Soc.* **1992**, 114, 6590.

The connecting link between the structural chemistry of lithium phosphides and the heavier alkali metal phosphides is their close structural similarity. The association trend observed in lithium phosphide chemistry, where the use of stoichiometric or substoichiometric amounts of donor led to an increased degree of oligomerization, can be nicely transferred to the heavier alkali metal analogues. By changing the size of the metal and keeping the ligand and donor constant, it is now possible to directly compare the influence of metal size on the association behavior. Immediately apparent is the polymeric composition of compounds **1a–c**, clearly representing an increased degree of oligomerization, as compared to the lithium analogues. However, this increased degree of association occurs only in one dimension with the lengthening of the ladder, even when the large Cs cation is employed. It is conceivable that the large steric requirement of the  $\text{P}(\text{SiMe}_3)_2$  ligand successfully prevents the polymerization into the third dimension. In addition, the ladder lengthening might also be explained on the basis of predominantly ionic interactions between metal and ligands, the strength of which decreases upon increase of the metal ionic radii. Accordingly, a larger ionic radius will not necessarily effect an increased degree of association, since additional alkali metal–ligand interactions will not result in significant lowering of the system enthalpy.

This view is further illustrated by analyzing the structural features of several related heavy alkali metal derivatives such as the ladder-type polymers  $[\text{K}(\text{thf})\text{SR}_f]_\infty$  ( $\text{R}_f = 2,4,6\text{-}(\text{CF}_3)_3\text{C}_6\text{H}_2$ )<sup>30b</sup> and  $[\text{KP}(\text{H})\text{Mes}^*]_\infty$ ,<sup>14</sup> where in part the large size of the ligand is responsible for the steric stabilization of the ladder-type aggregation pattern. This size argument is also supported by structural data obtained when smaller ligands, such as  $-\text{SCPh}_3$  or  $-\text{S-2,4,6-i-Pr}_3\text{C}_6\text{H}_2$ , were used in conjunction with sodium or potassium. In these cases, aggregation into the third dimension was observed under formation of hexameric, box-shaped, dimerized ladder fragments.<sup>30g,h</sup> Similar trends are also observed when the small primary amide  $\text{N}(\text{H})\text{SiMe}_3$  was used in conjunction with cesium: aggregation is observed under formation of the heterocubane  $[\text{CsN}(\text{H})\text{SiMe}_3]_4$ .<sup>32</sup> In contrast, the dimeric structures observed for the alkali metal terphenyl thiolates  $[\text{AS-2,6-}\{2,4,6\text{-i-Pr}_3\text{C}_6\text{H}_2\}_2\text{C}_6\text{H}_4]_2$  ( $\text{A} = \text{Li, Na, K, Rb, Cs}$ ) are retained throughout the entire alkali metal group.<sup>31</sup> It appears that there is a delicate balance between the steric requirement of the ligand and the strength of the ionic interaction between metal and ligand controlling the degree of association in these compounds.

The K–P bond lengths in **1a** (3.3169(7), 3.4063(8), and 3.4273(8) Å) are slightly longer than those in the primary phosphide  $[\text{KP}(\text{H})\text{Mes}^*]_\infty$  (3.181(20), 3.271(2), and 3.357(2) Å)<sup>14</sup> or in the dimeric  $[\text{K}(\text{thf})_2(2,4,6\text{-Me}_3\text{C}_6\text{H}_2)\text{Si}(\text{F})\text{-}t\text{-Bu}_2]_2$  (3.230(1) Å).<sup>15</sup> The K–P interactions also compare well with the K–P distances in  $\text{Cp}^*_2\text{ZrK}(\text{thf})_{1.5}\text{P}_3$  (3.37(1)–3.61(1) Å)<sup>16</sup> or  $\text{Cp}_2\text{ZrHK}(\text{thf})_2\text{PMes}^*$  (3.497(9) Å).<sup>17</sup> The K–P, Rb–P, and Cs–P bond lengths in **1a–c** increase relatively smoothly and correlate well with the ionic radii for the alkali metals. However, it is to note that the K–P bonds are slightly longer than expected from the trend in ionic radii.<sup>33</sup> The relatively long K–P interactions might be explained on the basis of the increased steric demand of the bis(trimethylsilyl) ligand onto

the relatively small potassium cation as compared to the larger rubidium or cesium centers. Clearly, the large metals are capable of accommodating the sterically demanding ligand without subsequent lengthening of the alkali metal–phosphorus contacts.

The retention of the ladder-type structure in **1a–c** gives an indication toward the reactivity of the target compounds whose reactivity increases dramatically upon descending the alkali metal group. The bis(trimethyl)silylphosphide ligand shields most effectively the potassium center, resulting in its reduced reactivity as compared to the rubidium or cesium analogue.

## Conclusions

This paper presents a convenient synthetic route toward heavy alkali metal phosphides. The reaction of trimethylsilyl-substituted phosphines with heavy alkali metal *tert*-butyl alcoholates results in the formation of exceptionally clean heavy alkali metal phosphides in excellent yields. The side product, a silyl protected alcohol, can be easily removed in a vacuum. The advantage of this route becomes apparent by comparing the much reduced reactivity of the starting materials required for this synthetic scheme with the reactivities of conventional primary or secondary phosphines and rubidium and cesium metal. The synthetic utility of this method is further underscored by the consistent isolation of monometalated products, even if the alkali metal reagents were employed in large excess.

The crystal structure analyses of compounds **1a–c** reveal their polymeric ladder-type structure, containing four coordinate alkali metal centers and five coordinate phosphorus atoms. The retention of this structure type, even if the size of the alkali metal center increases considerably, correlates with the observed increase in reactivity. Compounds **1a,b** react rapidly with oxygen and moisture, but the cesium derivative **1c** ignites spontaneously upon contact with air. This increase in reactivity can be related to the reduced steric shielding of the larger metal center by the ligand and donor. Experiments to explore the synthetic capabilities of these highly reactive reagents are currently under way.

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**Supporting Information Available:** X-ray crystallographic files, in CIF format, for all the structures are available on the Internet. Access information is given on any current masthead page.

## Note Added in Proof

After submission of this manuscript we became aware of the recent publication of a manuscript describing sodium and cesium phosphide interactions.<sup>34</sup>

IC9801950

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