Edith Alig, Isabelle Georg, Inge Sänger, Lothar Fink, Matthias Wagner and Hans-Wolfram Lerner*

Synthesis and structure of the donor-free potassium silanide K[SiPh$_3$]

https://doi.org/10.1515/znb-2018-0254
Received December 5, 2018; accepted December 15, 2018

Abstract: The donor-free potassium silanide K[SiPh$_3$] was prepared by the reaction of hexaphenyldisilane, Ph$_3$Si–SiPh$_3$, with potassium metal in benzene at room temperature. The solid-state structure, determined by powder X-ray diffraction consists of {K[SiPh$_3$]}$_2$ units, which interact with adjacent dimers to form an infinite chain along the crystallographic *c* axis (orthorhombic, space group *Cmc*2$_1$, $Z = 4$). The structure features short contacts between the π system of the phenyl rings and the potassium atoms of neighbouring K[SiPh$_3$] units.

Keywords: potassium; silanide; silyl anion; X-ray structure analysis.

1 Introduction

Silyl compounds of the alkali metals, also known as alkali metal silanides, have attracted considerable interest in the last decades [1–6]. Compounds with negatively charged silicon atoms are of fundamental importance in organometallic and inorganic synthesis. In particular, sterically encumbered organo-substituted silanides such as Li[Si(SiMe*t*Bu$_2$)$_3$] [7] or Na[SiMe(Si*t*Bu$_3$)$_2$] [8, 9] proved to be very useful σ-donating ligands. First papers regarding the synthesis and reactivity of silanides M[SiR$_3$] were published by Gilman et al. in the 1950s and 1960s [10, 11]. Examples studied in detail were the triphenylsilanides M[SiPh$_3$] (M = Li, Na, K, Rb, Cs) [12, 13]. Early syntheses used Ph$_3$Si–SiPh$_3$ as the starting material, which was treated with the respective alkali metal in liquid ammonia or in donor solvents [13, 14]. Very recently, the groups of Kleeberg and Okuda have synthesized a variety of donor-supported triphenylsilanides such as K(18-crown-6)(thf)$_n$[SiPh$_3$] ($n = 0, 1$) by Si–B or Si–Si bond cleavage reactions with K[O*t*Bu] (Scheme 1) [15–17]. Up to now unsupported triphenylsilanides M[SiPh$_3$] (M = Li, Na, K, Rb, Cs) have not been structurally characterized as far as we know.

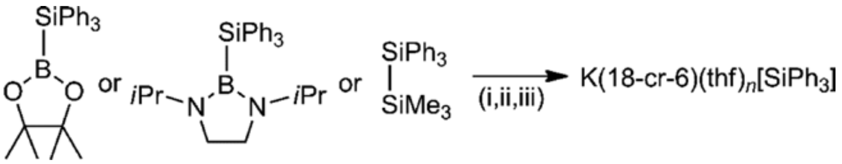
Our approach to the unsupported triphenylsilanide K[SiPh$_3$] was to cleave the Si–Si bond of Ph$_3$Si–SiPh$_3$ by treatment with potassium in apolar solvents. Here we report the synthesis and unusual structural features of the non-solvated potassium silanide K[SiPh$_3$]. The connectivity pattern as well as the geometry of the structure of K[SiPh$_3$] arise from strong interactions between the arene π systems and the potassium atoms.

2 Results and discussion

Given the interesting reactivity reported by Kleeberg and Okuda and our on-going interest in the chemistry of silanides, we have investigated the potassium-induced conversion of hexaphenyldisilane, Ph$_3$Si–SiPh$_3$. Our goal was to synthesize the donor-free potassium silanide K[SiPh$_3$]. As is shown in Scheme 2, addition of potassium to Ph$_3$Si–SiPh$_3$ in benzene and stirring the reaction mixture under argon for 7 days at room temperature quantitatively led to the formation of the silanide K[SiPh$_3$]. During the reaction the product precipitates from the solution. Generally, unsupported silanides such as K[SiPh$_3$] are poorly soluble in hydrocarbons. The product was analyzed by powder X-ray diffraction and NMR spectroscopy. The corresponding adduct K(thf)$_n$[SiPh$_3$] was quantitatively formed when K[SiPh$_3$] was treated with the donor solvent thf. In contrast to unsupported K[SiPh$_3$], the thf-complexed silanides K(thf)$_n$[SiPh$_3$] are soluble in common organic solvents and therefore can be examined by NMR spectroscopy. The potassium silanide K[SiPh$_3$] and its donor adducts are extremely sensitive to air and moisture.

The siloxide K[OSiPh$_3$] [18] is formed as a main product when K[SiPh$_3$] is exposed to air. For a plausible mechanism of this process see Ref. [19].

***Corresponding author: Hans-Wolfram Lerner,** Institut für Anorganische Chemie, Goethe-Universität Frankfurt am Main, Max-von-Laue-Straße 7, 60438 Frankfurt am Main, Germany, Fax: +49-69-79876329151, E-mail: lerner@chemie.uni-frankfurt.de
Edith Alig, Isabelle Georg, Inge Sänger, Lothar Fink and Matthias Wagner: Institut für Anorganische Chemie, Goethe-Universität Frankfurt am Main, 60438 Frankfurt am Main, Germany



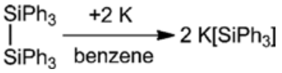
Scheme 1: Synthesis of the donor-supported triphenylsilanides K(18-crown-6)(thf)$_n$[SiPh$_3$] ($n=0, 1$) by Si–B or Si–Si bond cleavage reactions with K[O*t*Bu] in the presence of 18-crown-6 (18-cr-6); +K[O*t*Bu], +18-cr-6, in thf; (i) – pinBO*t*Bu (pin = pinacol) [15, 16]; (ii) – ((*i*PrN)$_2$(C$_2$H$_4$))BO*t*Bu [16]; (iii) – Me$_3$SiO*t*Bu [17].

The structure determination of unsupported K[SiPh$_3$] was performed by powder X-ray diffraction at two different temperatures. The molecular structure of the silanide is shown in Figs. 1–3. The compound crystallizes in the orthorhombic space group $Cmc2_1$ with $Z=4$. The molecule is located on a crystallographic mirror plane. Selected bond lengths and angles are listed in the caption of Fig. 1 and in Table 1. In the temperature range from −120 to +80°C no changes in constitution and symmetry or space group were observed. Crystal data and refinement details are given in Table 2.

The general structural motif of the silanide K[SiPh$_3$] features a ring formed by two silanide molecules (Fig. 2). This motif was also established in the crystal structures of Na(thf)[SiPh*t*Bu$_2$], K(thf)$_n$[SiPh*t*Bu$_2$] ($n=1$, 2), and K(C$_6$H$_6$)[SiMe(Si*t*Bu$_3$)$_2$] [21]. By contrast, unsolvated Na[SiPh*t*Bu$_2$] forms chains in the solid state [22].

The unit cell of K[SiPh$_3$] contains four formula units. As alluded above, the crystal structure consists of two K[SiPh$_3$] units, which interact with adjacent dimers {K[SiPh$_3$]}$_2$, to form an infinite chain along the crystallographic *c* axis (Fig. 3). The K atom is coordinated to one silicon atom and in η^6 fashion to three phenyl rings of two neighbouring silyl groups, as is shown in Fig. 2. Therefore, the K atoms possess the coordination number 19. The most characteristic features in the crystal structure of K[SiPh$_3$] are interactions between the metal atoms and the π systems of the phenyl rings. No agostic interactions have been observed.

In contrast to the polymeric structure of K[SiPh$_3$], the central framework of the solvent-free supersilanides



$$\underset{\text{SiPh}_3}{\overset{\text{SiPh}_3}{|}} \xrightarrow[\text{benzene}]{+2\text{ K}} 2\ \text{K[SiPh}_3]$$

Scheme 2: Synthesis of the donor-free potassium silanide K[SiPh$_3$].

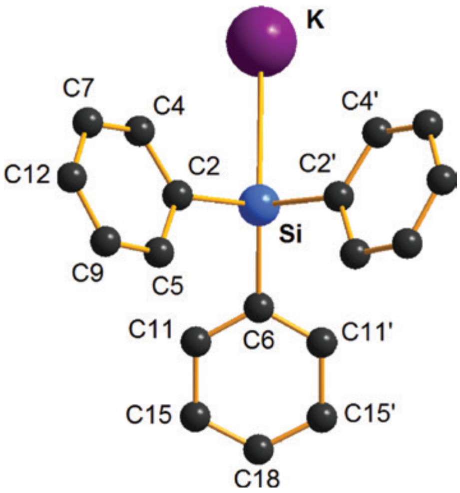


Fig. 1: Molecular structure of the donor-free potassium silanide K[SiPh$_3$] measured at $T=298$ K. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å), and bond angles (deg): Si–C(2) 2.020(5), Si–C(6) 1.966(6); C(2)–Si–C(6) 105.1(2), C(2)–Si–C(2′) 95.4(2). Symmetry-equivalent atoms (‘) were generated by applying the symmetry operator 1 – *x*, *y*, *z*.

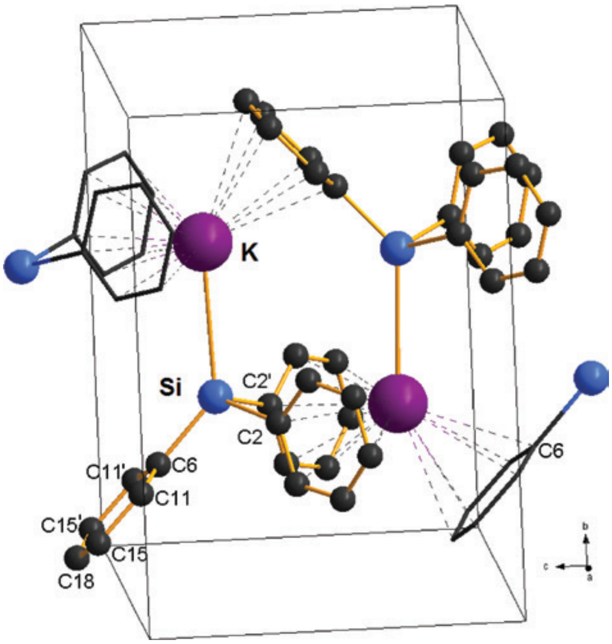


Fig. 2: Arrangement and connectivity of the dimers {K[SiPh$_3$]}$_2$ ($T=298$ K). View along the crystallographic *a* axis. Hydrogen atoms are omitted for clarity. For further atom numbering see Fig. 1. Intermolecular distances (Å): K(1) · · · COG1 3.028 Å, K(1) · · · COG2 2.918 Å; COG = center of gravity of the phenyl rings; COG1: C(2)C(4)C(5)C(7)C(9)C(12), COG2: C(6)C(11)C(15)C(18); symmetry operator of primed atoms: 1 – *x*, *y*, *z*.

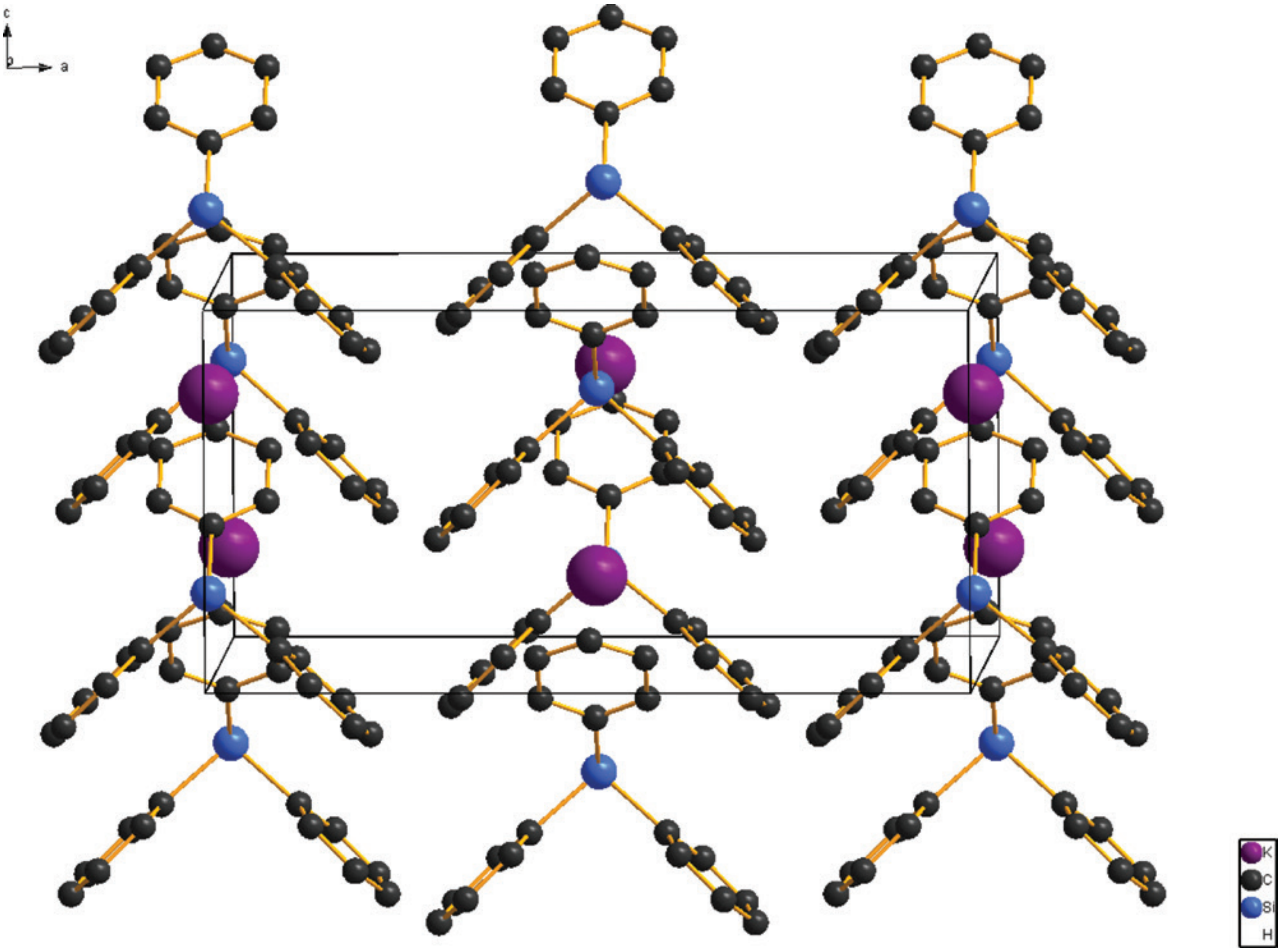


Fig. 3: Packing diagram of K[$SiPh_3$] (T = 298 K).

M[Si*t*Bu_3] (M = Li, Na) [23] and solvent-free hypersilanides M[Si($SiMe_3$)$_3$] (M = Li, Na, K) [24] forms a four-membered ring. Due to intermolecular CH–Na interactions, the very bulky silanide Na[SiMe(Si*t*Bu_3)$_2$] [9] displays a polymeric arrangement in the solid state.

The lengths of alkali metal-silicon bonds give evidence of the charge separation in silanides (Table 1). Generally, strong donors on the alkali metal center lengthen the Si–M bond and lead to more negative charge on the Si center. As is shown in Table 1, the crown-ether-supported silanide K(18-cr-6)[$SiPh_3$] possesses a shorter K–Si bond than the crown-ether-thf adduct K(18-cr-6)(thf)[$SiPh_3$]. Likewise both adducts K(18-cr-6)(thf)$_n$[$SiPh_3$] (n = 0, 1) possess longer Si–K bonds than the unsolvated potassium silanide K[$SiPh_3$] (cf. Table 1). Due to the bulky *tert*-butyl groups, the sum of the C–Si–C angles for K(C_6D_6)$_3$[Si*t*Bu_3] (Σ C–Si–C: 317.9(1)°) [23] is significantly greater than those determined for the structures of the potassium triphenylsilanides (cf. Table 1).

Table 1: Geometric parameters of potassium triphenylsilanides.

	Si–K (Å)	Si–C (Å)[a]	ΣC–Si–C (deg)	Reference
K[$SiPh_3$]	3.458(5)	1.994(6)	295.6(2)	This work
K(18-cr-6)[$SiPh_3$]	3.540(1)	1.929(1)	297.0(6)	[11]
K(18-cr-6)(thf)[$SiPh_3$]	3.635(1)	1.935(4)	306.8(2)	[12]

[a] Average values.

In summary, the synthesis of unsupported K[$SiPh_3$] was achieved by the reaction of Ph_3Si–$SiPh_3$ with potassium in benzene at room temperature. The silanide K[$SiPh_3$] could be isolated in good yield and high purity by this procedure. Therefore, alkali metal-induced Si–Si bond cleavage of Ph_3Si–$SiPh_3$ gives a convenient access to unsupported triphenylsilanides. The solid-state structure of unsupported K[$SiPh_3$] consists of dimers {K[$SiPh_3$]}$_2$, which interact with adjacent dimers to form an infinite chain along the crystallographic c axis. In detail, the structure reveals short contacts between the π systems of the phenyl rings and the potassium atoms of neighbouring K[$SiPh_3$] units.

Table 2: Crystal and structure refinement data of K[SiPh$_3$] at $T = 298$ K and 153 K.

	K[SiPh$_3$]	K[SiPh$_3$]
Temperature, K	298	153
Formula	$C_{18}H_{15}SiK$	$C_{18}H_{15}SiK$
M_r	298.15	298.15
Crystal size, mm^3	Powder	Powder
Crystal system	Orthorhombic	Orthorhombic
Space group	$Cmc2_1$	$Cmc2_1$
a, Å	16.5948(5)	16.3678(9)
b, Å	11.6568(3)	11.5455(6)
c, Å	8.32999(16)	8.2963(3)
V, Å^3	1611.37(7)	1567.79(13)
Z	4	4
$D_{calcd.}$, g cm^{-3}	1.23	1.27
μ(Cu$K\alpha$), mm^{-1}	3.4	3.5
F(000), e	624.0	624.0
hkl range	13, 9, 6	13, 9, 6
$((\sin\theta)/\lambda)_{max}$, Å^{-1}	0.417	0.417
Refl. measured	514	498
Refl. unique	286	277
R_{int}	0.0155	0.0168
Param. refined	97	97
R_p/R_{wp} ^{a}	0.0256/0.0354	0.0457/0.0637
R_{exp} ^{a}	0.0340	0.0406
GoF^a	1.043	1.569

^{a}R values and GoF according to TOPAS [20]: $R_p = \Sigma|Y_o - Y_c|/\Sigma Y_o$; $R_{wp} = \{\Sigma[w(Y_o - Y_c)^2/\{\Sigma wY_o^2)\}^{0.5}$, $R_{exp} = \{\Sigma M - P/\Sigma wY_o^2)\}^{0.5}$; $R_{int} = \Sigma|I_o - I_c|/\Sigma I_o$; GoF $= \{\Sigma[w(Y_o - Y_c)^2]/(M - P)\}^{0.5}$; $w = 1/\sigma(Y_o)^2$ with M the number of data points, P the number of parameters.

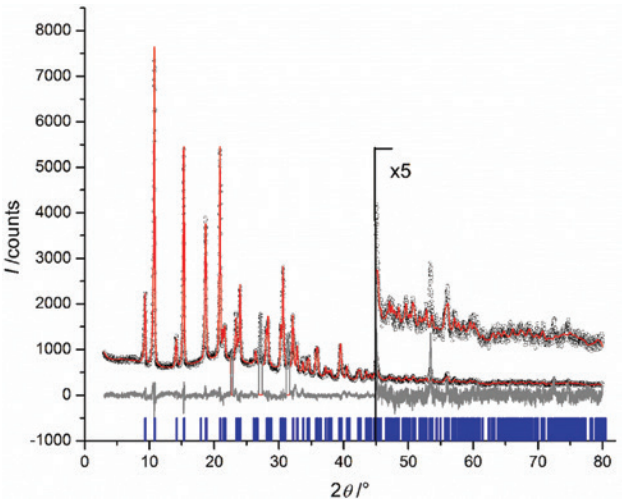


Fig. 4: Rietveld plot of the donor-free potassium silanide K[SiPh$_3$] measured at $T = 153$ K. Color code: Black circles $= I_{obs}$; red line $= I_{calc}$; grey line $= I_{obs} - I_{calc}$; blue ticks = reflection positions. Excluded regions at $2\theta = 27.2$ and 31.4° are due to traces of impurity and at 22.7° due to icing of the capillary.

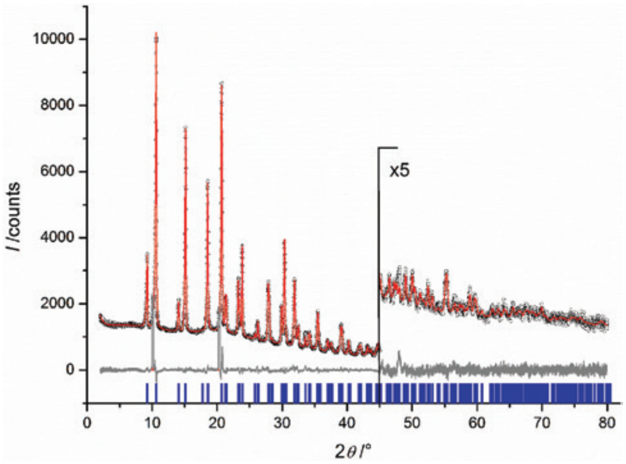


Fig. 5: Rietveld plot of the donor-free potassium silanide K[SiPh$_3$] measured at $T = 298$ K. Color code: Black circles $= I_{obs}$; red line $= I_{calc}$; grey line $= I_{obs} - I_{calc}$; blue ticks = reflection positions. Excluded regions at $2\theta = 10.1$ and 20.2° are due to traces of the starting material.

3 Experimental section

The solvents thf, thf-d_8, benzene, and C_6D_6 were stirred over sodium/benzophenone and distilled prior to use. $Ph_3Si–SiPh_3$ was prepared according to the published procedure [25]. All other starting materials were purchased from commercial sources and used without further purification. The NMR spectra were recorded on Bruker Avance 300, Avance 400, and Avance 500 spectrometers. NMR chemical shifts are reported in ppm. Abbreviations: s = singlet; m = multiplet. Elemental analyses were carried out by the Microanalytical Laboratory of the Goethe University Frankfurt.

3.1 Synthesis of potassium triphenylsilanide K[SiPh$_3$]

(a) A mixture of $Ph_3Si–SiPh_3$ [25] (1.00 g, 1.93 mmol) and potassium pieces (0.29 g, 7.49 mmol) in benzene (11 mL) was stirred at room temperature under argon for 1 week. After removing the remaining K pieces, the formed precipitate was separated by filtering. The colorless solid was washed with benzene and dried *in vacuo*. The product was analyzed by powder X-ray diffraction (cf. Fig. 4) and by NMR spectroscopy after dissolution in thf (below) (yield: 1.13 g, 98%). – Anal. for $C_{18}H_{15}KSi$ (298.5) calcd. C 72.43, H 5.07; found C 68.20, H 5.11. The discrepancy in the carbon content is probably due to carbide formation (the analysis was done without additives).

(b) A mixture of $Ph_3Si–SiPh_3$ [25] (10.26 g, 19.78 mmol) and potassium pieces (1.50 g, 36.36 mmol) in benzene (200 mL) was stirred at room temperature under argon for 1 week. The formed precipitate was separated by filtering. The colorless solid was washed with benzene and dried *in vacuo*. The product was analyzed by powder X-ray diffraction (cf. Fig. 5). Peaks of the starting material $Ph_3Si–SiPh_3$ were also detected. The analysis of the Rietveld plot indicates 96% of K[SiPh$_3$] with 4% of $Ph_3Si–SiPh_3$ as impurity.

(c) To K[SiPh$_3$] (0.03 g, 0.1 mmol) 1 mL thf was added at room temperature. The $^1H/^{13}C/^{29}Si$ NMR spectra exclusively revealed the signals of the thf-supported silanide K(thf)$_n$[SiPh$_3$]. – ^1H NMR (300 MHz, thf-d_8): $\delta = 7.38–7.34$ (m, 6 H, *o*-CHAr), 6.90–6.85 (m, 6 H, *m*-CHAr), 6.77–6.71 (m, 3 H, *p*-CHAr), 3.54 (m, OCH$_2$), 1.72 (m, CH$_2$). $^{13}C\{^1H\}$ NMR (126 MHz, thf-d_8): $\delta = 160.8$ (*ipso*-CAr), 131.1 (*o*-CHAr), 126.4 (*m*-CHAr), 123.0 (*p*-CHAr), 71.0 (OCH$_2$), 25.4 (CH$_2$). – $^{29}Si\{^1H\}$ NMR (59.6 MHz, thf-d_8): $\delta = -7.1$ (s).

(d) A solution of K[SiPh$_3$] (0.05 mmol) in 0.5 mL thf-d_8 was kept in air for 3 h at room temperature. The $^1H/^{13}C/^{29}Si$ NMR spectra revealed signals which can be attributed to K[OSiPh$_3$] [18]. Additionally, signals of the side-products, Ph_3SiH and Ph_3SiOH, were observed.

3.2 Crystal structure determinations

The X-ray powder diffraction experiments were performed on a STOE Stadi-P diffractometer equipped with a Ge(111) monochromator and a linear position-sensitive detector (PSD) using Cu$K\alpha_1$ radiation ($\lambda = 1.54056$ Å). The specimen was measured in a sealed borosilicate glass capillary with a diameter of 1.0 mm. The data was collected with the STOE WinXPOW software [26].

Temperature-dependent XRPD measurements were performed on an identical STOE Stadi-P diffractometer equipped with an Oxford Cryosystem 700. The measurements were carried out in a sealed 1.0 mm glass capillary under nitrogen.

3.3 Structure determinations from X-ray powder data

The powder patterns were indexed with Dicvol91 [27]. The space group determination was carried out in Dash [28]. The structures were solved with a starting molecular structural model in direct space using simulated annealing in Dash. Rietveld refinements were performed with Topas [20]. First, a Pawley refinement was carried out to refine background, zero point error, unit cell parameters, peak width, and peak asymmetry parameters. In the Rietveld refinements, the phenyl rings including H atoms were restrained to be flat; the bond lengths and bond angles in the rings were restrained to meaningful values. The values of the isotropic displacement parameters of the hydrogen atoms were constrained to be 1.2 times of those of the atoms to which they are attached. K and Si were not restrained. Two regions at $2\theta = 10.1$ and 20.2° were excluded due to traces of the starting material.

CCDC 1883105 (K[SiPh$_3$] at $T = 298$ K) and 1883106 (K[SiPh$_3$] at $T = 153$ K) 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.

References

[1] P. D. Lickiss, C. Smith, *Coord. Chem. Rev.* **1995**, *145*, 75.
[2] K. Tamao, A. Kawachi, *Adv. Organomet. Chem.* **1995**, *38*, 1.
[3] N. Wiberg, *Coord. Chem. Rev.* **1997**, *163*, 217.
[4] J. Belzner, U. Dehnert, *The Chemistry of Organic Silicon Compounds*, Vol. 2, (Eds.: Z. Rappoport, Y. Apeloig), Wiley, Chichester, **1998**, p. 779.
[5] H.-W. Lerner, *Coord. Chem. Rev.* **2005**, *249*, 781.
[6] C. Marschner, *Silicon-Centered Anions* in *Organosilicon Compounds. Theory and Experiment (Synthesis)*, Vol. 1, (Ed.: V. Y. Lee), Academic Press, Oxford, **2017**, chapter 7, pp. 295–360.
[7] M. Nakamoto, T. Fukawa, V. Y. Lee, A. Sekiguchi, *J. Am. Chem. Soc.* **2002**, *124*, 15160.
[8] N. Wiberg, W. Niedermayer, H. Nöth, M. Warchhold, *J. Organomet. Chem.* **2001**, *628*, 46.
[9] I. Sänger, M. Gärtner, M. Bolte, M. Wagner, H.-W. Lerner, *Z. Anorg. Allg. Chem.* **2018**, *644*, 925.
[10] H. Gilman, T. C. Wu, H. A. Hartzfeld, G. A. Guter, A. G. Smith, J. J. Goodman, S. H. Eidt, *J. Am. Chem. Soc.* **1952**, *74*, 561.
[11] H. Gilman, T. C. Wu, *J. Am. Chem. Soc.* **1951**, *73*, 4031.
[12] R. A. Benkeser, R. G. Severson, *J. Am. Chem. Soc.* **1951**, *73*, 1424.
[13] M. V. George, D. J. Peterson, H. Gilman, *J. Am. Chem. Soc.* **1960**, *82*, 403 and ref. cited therein.
[14] E. Wiberg, O. Stecher, H. J. Andraschek, L. Kreuzbichler, E. Staude, *Angew. Chem. Int. Ed. Engl.* **1963**, *2*, 507.
[15] C. Kleeberg, C. Borner, *Eur. J. Inorg. Chem.* **2013**, 2799.
[16] C. Kleeberg, *Dalton Trans.* **2013**, *42*, 8276.
[17] V. Leich, K. Lamberts, T. P. Spaniol, J. Okuda, *Dalton Trans.* **2014**, *43*, 14315.
[18] M. J. McGeary, K. Folting, W. E. Streib, J. C. Huffman, K. G. Caulton, *Polyhedron* **1991**, *10*, 2699.
[19] A. Budanow, H. Hashemi Haeri, I. Sänger, F. Schödel, M. Bolte, T. Prisner, M. Wagner, H.-W. Lerner, *Chem. Eur. J.* **2014**, *20*, 10236.
[20] A. Coelho, Topas Acad., *User Man. Tech. Ref.* Brisbane (Australia) **2009**.

[21] H.-W. Lerner, S. Scholz, M. Bolte, M. Wagner, *Z. Anorg. Allg. Chem.* **2004**, *630*, 443.

[22] H.-W. Lerner, S. Scholz, M. Bolte, *Z. Anorg. Allg. Chem.* **2001**, *627*, 1638.

[23] N. Wiberg, K. Amelunxen, H.-W. Lerner, H. Schuster, H. Nöth, I. Krossing, M. Schmidt-Amelunxen, T. Seifert, *J. Organomet. Chem.* **1997**, *542*, 1.

[24] K. W. Klinkhammer, *Chem. Eur. J.* **1997**, *3*, 1418.

[25] T. Bernert, B. Winkler, Y. Krysiak, L. Fink, M. Berger, E. Alig, L. Bayarjargal, V. Milman, L. Ehm, P. W. Stephens, N. Auner, H.-W. Lerner, *Cryst. Growth Des.* **2014**, *14*, 2937.

[26] WinXPOW 210, STOE & Cie GmbH, Darmstadt (Germany) **2004**.

[27] A. Boultif, D. Louër, *J. Appl. Crystallogr.* **1991**, *24*, 987.

[28] W. I. F. David, K. Shankland, J. van de Streek, E. Pidcock, W. D. S. Motherwell, J. C. Cole, *J. Appl. Crystallogr.* **2006**, *39*, 910.