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Formation of α -[KSiH₃] by hydrogenolysis of potassium triphenylsilyl

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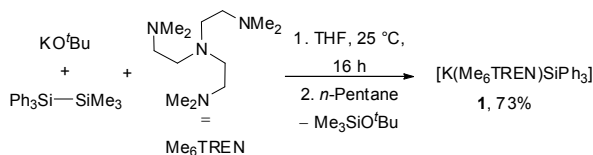
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Hydrogenation of easily accessible potassium triphenylsilyl [K(Me₆TREN)SiPh₃] gave the hydrogen storage material α -[KSiH₃] in high yields by an unusual hydrogenolytic cleavage of silicon-phenyl bonds.

Metal hydrides are of current interest as hydrogen storage materials, as dihydrogen is considered to be the ideal energy carrier.¹ Compounds suitable for hydrogen storage are required to have defined thermodynamic properties for hydrogenation and dehydrogenation (enthalpy of hydrogenation \sim 40 kJ mol⁻¹) as well as show reversibility of hydrogen storage under mild conditions (1–10 bar at temperatures of -40 – 100 °C).² Recently, the system KSi/ α -[KSiH₃] was reported by Janot et al. to be capable of reversibly storing 4.3 wt-% of dihydrogen within a promising pressure–temperature window.³ Originally, α -[KSiH₃] was obtained by reduction of monosilane SiH₄ with potassium metal at reaction times up to 76 days.⁴ Handling of SiH₄ is extremely hazardous and therefore hydrogenation (5 MPa at 100 °C) of the Zintl phase potassium silicide KSi to form α -[KSiH₃] is an elegant synthetic approach.³ Here we report a solution approach to α -[KSiH₃] by hydrogenation of potassium triphenylsilyl [K(Me₆TREN)SiPh₃] under ambient reaction conditions. This unexpected formation appears to be assisted by the tripodal amine Me₆TREN (tris{2-(dimethyl-amino)ethyl}amine).⁵



Scheme 1 Synthesis of potassium triphenylsilyl **1** from Ph₃SiSiMe₃ and Me₆TREN.

Following a published procedure⁶ potassium triphenylsilyl was generated by reacting potassium *tert*-butoxide with 1,1,1-trimethyl-2,2,2-triphenyldisilane⁷ and trapped with Me₆TREN^{5a} as [K(Me₆TREN)SiPh₃] (**1**). It was isolated in moderate yields as orange crystals, soluble in THF and benzene, but insoluble in saturated hydrocarbons (Scheme 1). Single crystals of **1** were obtained from saturated THF solutions upon cooling to -30 °C. Results of an X-ray diffraction study showed the presence of a contact ion pair in the crystal lattice (Figure 1).

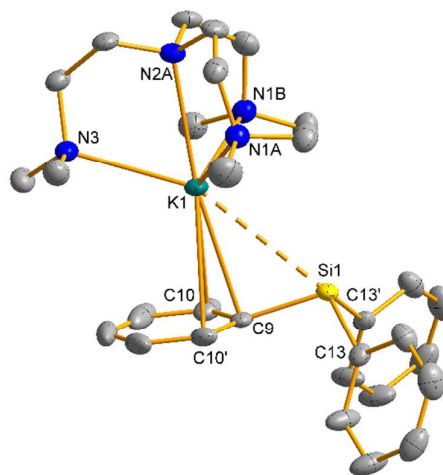


Figure 1 Molecular structure of **1**. Displacement ellipsoids are shown at the 50% probability level; hydrogen atoms are omitted for clarity. The disordered atoms of the Me₆TREN ligand are only shown with one split position. Selected interatomic distances [Å] and angles [°]: K1–Si1 3.5594(8), K1–N1B 2.761(4), K1–N1A 2.840(4), K1–N3 2.834(2), K1–N2A 2.895(3), K1–C9 3.026(2), K1–C10/C'10 3.1965(18), C9–C10/C'10 1.408(2), C10–C9–C10' 115.0(2), Si1–K1–N2A 139.07(6), Si1–C9–C10–C11 165.66(15), Si1–C13–C14–C15 178.28(15).

1 crystallized in the orthorhombic space group *Pnma* with crystallographically imposed mirror symmetry leading to disorder of the Me₆TREN ligand that could be resolved well with split positions. The Me₆TREN ligand is coordinated in a κ^4N manner at the potassium cation with K1–N1–3 bond lengths of 2.761(4)–2.895(3) Å. The potassium cation shows an

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η^3 coordination to the *ipso/ortho*-carbon atoms with bond lengths of K1–C9 of 3.026(2) Å and K1–C10/C'10 of 3.1965(18) Å. Bond distances and angles are comparable to those in $[\text{K}(\text{Me}_6\text{TREN})\text{CH}_2\text{Ph}]$,^{5c} $[\text{K}(\text{Me}_6\text{TREN})\text{CH}_2(\text{Ph}-3,5\text{-Me}_2)]$ ⁸ and potassium allyl (allyl = C_3H_5) complexes.⁹ A strong $\text{K}\cdots\text{Ph}$ interaction is reflected by one of the three phenyl groups being significantly distorted (Figure 1). The silicon atom is dislocated by 0.406(3) Å from the plane formed by the phenyl carbon atoms C9–C12. This type of bending was explained by electronic effects for lithium silyls¹⁰ for which similar distortions of the $(\text{SiPh}_3)^-$ anions were observed.¹¹ The interatomic distance $\text{K1}\cdots\text{Si1}$ of 3.5594(8) Å is in the range of other $\text{K}\cdots\text{Si}$ distances (3.460(3)–3.635(1) Å).^{11a, 12}

Table 1 Selected ^1H and $^{29}\text{Si}\{^1\text{H}\}$ NMR chemical shifts in THF-D_8 at 25 °C of the silyl complexes.

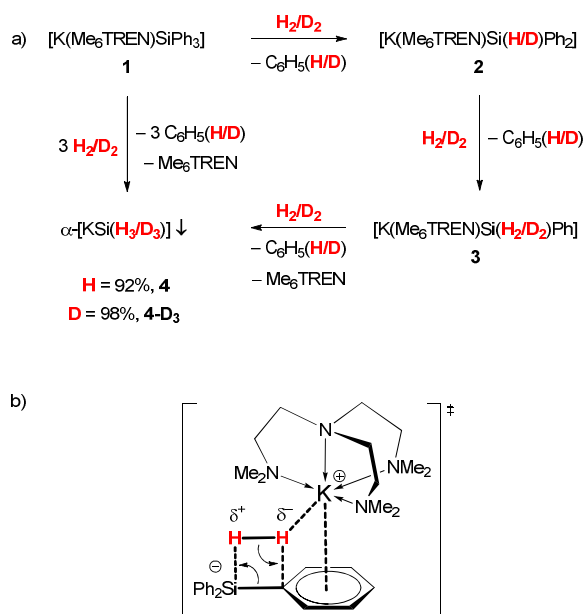
Entry	Comp.	δ_{H} [ppm]			Si–H [Hz]	δ_{Si} [ppm]
		<i>ortho</i> -Ph	<i>meta</i> -Ph	<i>para</i> -Ph		
1	1	7.33	6.92	6.81	–	–7.38
2	2	7.52	6.88	6.74	4.53	–25.37
3	3	7.46	6.78	6.65	3.37	–82.26
4	4	–	–	–	1.25	76.4
5	KSiH_3^{13}	–	–	–	1.17	77

The ^1H NMR spectrum of **1** in THF-D_8 at 25 °C shows one singlet at $\delta = 2.14$ ppm for the CH_3 protons and four AA'XX' doublets at $\delta = 2.28$ –2.54 ppm for each CH_2 proton of the Me_6TREN ligand (ratio 18:3:3:3). The triphenylsilyl anion shows three multiplets in the range of $\delta = 6.77$ –7.37 ppm for the aromatic protons in the ^1H NMR spectrum. The $^{29}\text{Si}\{^1\text{H}\}$ NMR spectrum of **1** shows one singlet at $\delta = -7.38$ ppm and is in the range of known potassium silyls (see ESI).^{11a, 12b} VT ^1H NMR spectra of $[\text{K}(\text{Me}_6\text{TREN})\text{SiPh}_3]$ (**1**) in THF-D_8 did not indicate η^3 coordination of the phenyl group at the potassium cation. Even at -95 °C the ^1H NMR spectra of **1** shows only one set of signals for the three sets of the aromatic protons, suggesting that the exchange rate between the different phenyl groups is fast on the NMR time scale (as a result of dissociation).

A solution of $[\text{K}(\text{Me}_6\text{TREN})\text{SiPh}_3]$ (**1**) in THF-D_8 was reacted with H_2 (1 bar) at 25 °C. After 12 h the ^1H NMR spectrum shows a new hydride resonance at $\delta = 4.53$ ppm ($^1J_{\text{SiH}} = 96.5$ Hz) and a new set of aromatic resonances at $\delta = 6.74$ –7.52 ppm (Table 1, entry 2). These resonances were assigned to a hydridodiphenylsilyl anion $(\text{SiHPh}_2)^-$, comparable to those of lithium silyl $[\text{LiSiHMe}_2(\text{THF})_2]$ (Mes = mesityl group).¹⁴ Additionally, a stoichiometric amount of benzene ($\delta = 7.13$ ppm) was observed in the ^1H NMR spectrum. The $^{29}\text{Si}\{^1\text{H}\}$ NMR spectrum showed a new resonance at $\delta = -25.37$ ppm, corresponding to the silyl anion $(\text{SiHPh}_2)^-$ (see ESI). We assume hydrogenolytic cleavage of silicon-phenyl bond in $[\text{K}(\text{Me}_6\text{TREN})\text{SiPh}_3]$ (**1**) giving $[\text{K}(\text{Me}_6\text{TREN})\text{SiHPh}_2]$ (**2**) and benzene.

After 48 h at 25 °C a similar set of signals along with another equivalent of benzene were observed in the ^1H and $^{29}\text{Si}\{^1\text{H}\}$ NMR spectra, which were assigned to a dihydrido-phenylsilyl anion $(\text{SiH}_2\text{Ph})^-$ (Table 1, entry 3). After 72 h an off-white powder precipitated from the reaction mixture and the ^1H NMR spectrum shows an additional hydride resonance at $\delta = 1.25$ ppm ($^1J_{\text{SiH}} = 76.4$ Hz), assigned to the trihydridosilyl anion $(\text{SiH}_3)^-$ (Table 1, entry 4). The $^{29}\text{Si}\{^1\text{H}\}$ NMR chemical shift at $\delta = -169.1$ ppm agrees with that of $[\text{KSiH}_3]$ ¹³ ($\delta = -165$ ppm, $^1J_{\text{SiH}} = 77$ Hz) and $[\text{K}(18\text{-crown-6})\text{SiH}_3]$ ¹⁵ ($\delta = -169.4$ ppm, $^1J_{\text{SiH}} = 73.64$ Hz). After 7 d at 25 °C, **1** is fully consumed and α - $[\text{KSiH}_3]$ (**4**) as off-white powder precipitated from the reaction mixture (for ^1H and $^{29}\text{Si}\{^1\text{H}\}$ NMR spectra, see ESI).

On a preparative scale quantitative yields of α - $[\text{KSiH}_3]$ (**4**) or α - $[\text{KSiD}_3]$ (**4-D**₃) were obtained when D_2 (1 bar) was used. The formation of **4** and **4-D**₃ was confirmed by powder X-ray diffraction, IR spectroscopy ($\nu_{\text{SiH}}/\nu_{\text{SiD}} = 1.38$)¹⁶ and NMR spectroscopy (see ESI). The powder diffraction patterns and IR data compared well to those reported for cubic α - $[\text{KSiH}_3]$ and α - $[\text{KSiD}_3]$.^{16–17} The NaCl-type compounds α - $[\text{KSiH}_3]/\alpha$ - $[\text{KSiD}_3]$ are sparingly soluble in THF and crystallized from the reaction mixture.



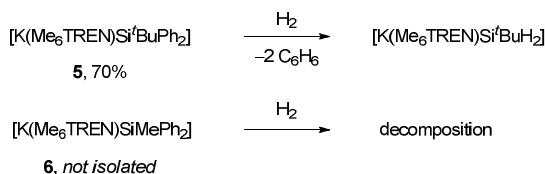
Scheme 2 a) Stepwise hydrogenolysis of potassium silyl $[\text{K}(\text{Me}_6\text{TREN})\text{SiPh}_3]$ (**1**) across the Si-C_{Ph} bond. b) Proposed transition state for the silicon-phenyl bond cleavage by dihydrogen.

GC/MS analysis of the supernatant THF solutions showed the presence of C_6H_6 ($m/z = 78$ (M^+)) in the case of the reaction with H_2 . Only $\text{C}_6\text{H}_5\text{D}$ ($m/z = 79$ (M^+)) was obtained using D_2 . These findings support the proposed reaction pathway (Scheme 2) and the selectivity of the hydrogenolysis. Notably, other potassium triphenylsilyls such as $[\text{K}(18\text{-crown-6})(\text{THF})\text{SiPh}_3]$ ^{11a} or $[\text{K}(\text{THF})\text{SiPh}_3]$ ^{11b, 12} in the presence of neutral amines pmdta, tmeda or crypt-222 did not react with dihydrogen as did the Me_6TREN adduct **1**. The presence of

stoichiometric amount of Me₆TREN appears to be unique in assisting the hydrogenolysis across the silicon-phenyl bond.

On the basis of this observation, we propose a hydrogenolytic cleavage of the silicon-phenyl bond to form the corresponding hydridosilyl anion and benzene *via* the transition state depicted in Scheme 2b). The reaction proceeds stepwise under mild conditions and does not go through the hypervalent (i.e. five-coordinate) hydridosilyl anion transition state.¹⁸ Spectroscopic data of hypervalent hydridosilyl anions are known, but we never detected these anions in the reaction mixtures.¹⁹ σ -Bond metatheses of a silicon-phenyl bond, catalyzed by lanthanide and hafnium complexes, were previously observed for phenylsilane.²⁰

To probe the possibility of cleaving a silicon-alkyl bond, we prepared [K(Me₆TREN)Si^tBuPh₂] (**5**) and [K(Me₆TREN)SiMePh₂] (**6**). **5** was prepared in analogy to [K(Me₆TREN)SiPh₃] (**1**) and isolated in 70% yield, whilst **6** was synthesized *in situ* and characterized by ¹H NMR spectroscopy. **5** shows similar ¹H, ¹³C{¹H} and ²⁹Si{¹H} NMR spectra and solubility properties as **1** (see ESI).



Scheme 3. Hydrogenation of **5** and **6**.

The potassium silyl **5** reacted with dihydrogen (1 bar) in THF-D₈ selectively. After 4 h the ¹H NMR spectrum at 25 °C showed a new hydride resonance at $\delta = 3.70$ ppm (¹J_{SiH} = 89.0 Hz) together with a new set of aromatic resonances at $\delta = 6.73$ -7.36 ppm and stoichiometric amount of benzene (see ESI for ¹H and ²⁹Si{¹H} NMR spectra). In the ²⁹Si{¹H} NMR a new resonance at $\delta = 2.01$ ppm was observed. The ¹H and ²⁹Si{¹H} NMR resonances were assigned to [K(Me₆TREN)Si^tBuPH]. After 28 h another phenyl group was cleaved to give [K(Me₆TREN)Si^tBuH₂]. Although the starting material **5** was consumed after 48 h, no resonances of **4** were detected. Due to rapid decomposition [K(Me₆TREN)Si^tBuPH] or [K(Me₆TREN)Si^tBuH₂] could not be isolated. For [K(Me₆TREN)SiMePh₂] (**6**) no selective reaction was observed.

In conclusion, we have found that potassium silyls [K(Me₆TREN)SiPh₃] (**1**) reacted with dihydrogen under ambient conditions with cleavage of silicon-phenyl bonds to give the corresponding hydridosilyl compounds and benzene, eventually resulting in the formation of crystalline α -[KSiH₃]. Notably, no formation of KH was observed. In contrast, the hydrogenolysis of the calcium bis(triphenylsilyl) [Ca(SiPh₃)₂(THF)₄] gave calcium dihydride.^{11c} In order to better understand the dichotomy of metal hydride versus silicon hydride formation, we continue studying the hydrogenolysis of other alkali and earth alkaline metal silyls.

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