

## Hydrogen Storage

## Alkali Metal Triphenyl- and Trihydridosilanides Stabilized by a Macrocyclic Polyamine Ligand

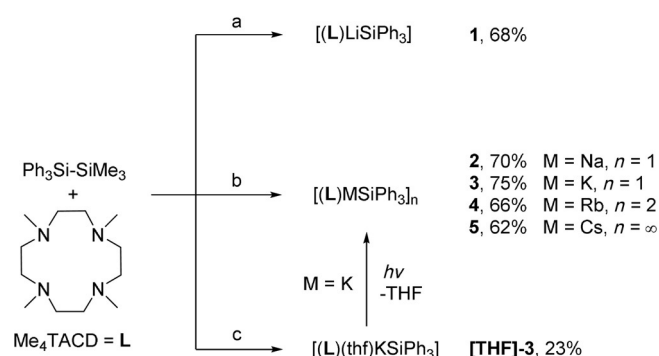
Danny Schuhknecht,<sup>[a]</sup> Valeri Leich,<sup>[a]</sup> Thomas P. Spaniol,<sup>[a]</sup> Iskander Douair,<sup>[b]</sup> Laurent Maron,<sup>[b]</sup> and Jun Okuda\*<sup>[a]</sup>

**Abstract:** Potassium silanide  $[\text{KSiH}_3]_\infty$  contains 4.2 wt% of hydrogen and has been intensely studied as hydrogen storage material. The macrocyclic ligand  $\text{Me}_4\text{TACD}$  (1,4,7,10-tetramethyl-1,4,7,10-tetraaminocyclododecane, **L**) stabilizes the full range of triphenylsilyl complexes  $[(\text{L})\text{MSiPh}_3]_n$  ( $\text{M} = \text{Li} - \text{Cs}$ ), which react with  $\text{H}_2$  or  $\text{PhSiH}_3$  to form molecular  $[(\text{L})\text{MSiH}_3]_n$  that can be isolated in soluble form and fully characterized.

Metal hydrides are of current interest as hydrogen storage material, because  $\text{H}_2$  is considered as the only carbon-free energy carrier.<sup>[1]</sup> Suitable storage materials require defined thermodynamic properties of hydrogenation and dehydrogenation (enthalpy of hydrogenation  $-40 \text{ kJ mol}^{-1}$ ), as well as reversibility of hydrogen storage under mild conditions (1–10 bar at temperatures of 40–100 °C).<sup>[2]</sup> The alkali metal silanides  $[\text{MSiH}_3]_\infty$  contain high wt% of hydrogen ( $\text{M} = \text{Li}$ , 7.95;  $\text{Na}$ , 5.59;  $\text{K}$ , 4.31) and for the heavier  $\text{K} - \text{Cs}$  salts, reversible uptake and release of  $\text{H}_2$  has been shown.<sup>[3]</sup> They can be synthesized by treating metal or metal alloys with hazardous  $\text{SiH}_4$  or  $\text{PhSiH}_3$ ,<sup>[4]</sup> or more conveniently, by hydrogenolysis of the Zintl phase  $\text{MSi}$ .<sup>[3,5]</sup> The lighter  $[\text{LiSiH}_3]_\infty$  and  $[\text{NaSiH}_3]_\infty$  are less thermodynamically stable and not accessible from the Zintl phases that form stable  $\text{MH}$  and  $\text{M}_2\text{Si}$ , upon hydrogenolysis.<sup>[3b,6]</sup> Only few molecular complexes containing  $[\text{SiH}_3]^-$  anions have been isolated from reactions involving  $\text{SiH}_4$  and studied in solution and in solid state.<sup>[4b,7]</sup> Alkali and alkaline earth metal silanides catalyze such reactions as hydrofunctionalization of olefins and pyridine,<sup>[8]</sup> and are also active in the defluorination of organofluorides.<sup>[9]</sup> Recently, we showed that the molecular complex

$[(\text{Me}_6\text{TREN})\text{KSiPh}_3]$  reacts with  $\text{H}_2$  to give a soluble form of  $[\alpha\text{-KSiH}_3]_\infty$ .<sup>[10]</sup> Herein, we report the synthesis of the full range of alkali metal triphenylsilylanides stabilized by the macrocyclic ligand  $\text{Me}_4\text{TACD}$  (1,4,7,10-tetramethyl-1,4,7,10-tetraaminocyclododecane, **L**) and their reactivity towards  $\text{H}_2$  and  $\text{PhSiH}_3$  to form molecular trihydridosilanides  $[(\text{L})\text{MSiH}_3]_n$ .

Similar to previously reported crown ether adducts,<sup>[8b]</sup>  $\text{Me}_4\text{TACD}$  stabilized alkali metal triphenylsilylanides  $[(\text{L})\text{MSiPh}_3]$  ( $\text{M} = \text{Li} - \text{Cs}$ , 1–5) were synthesized from the reaction of disilane  $\text{Ph}_3\text{Si-SiMe}_3$  with  $[\text{MOTBu}]$  ( $\text{M} = \text{Na} - \text{Cs}$ ) or in the case of lithium, with the more basic alkyl  $[\text{LiCH}_2\text{SiMe}_3]$  (Scheme 1). In all cases,



**Scheme 1.** Synthesis of alkali metal triphenylsilylanides  $[(\text{L})\text{MSiPh}_3]$ .

a) 1.  $[\text{LiCH}_2\text{SiMe}_3]$ , THF, 25 °C,  $(\text{Me}_3\text{Si})_2\text{CH}_2$ ; 2. THF/*n*-pentane,  $-30^\circ\text{C}$ .  
b) 1.  $[\text{MOTBu}]$  ( $\text{M} = \text{Na}$ ,  $\text{K}$ ,  $\text{Rb}$ ,  $\text{Cs}$ ), THF, 25 °C,  $t\text{BuOSiMe}_3$ ; 2. THF/*n*-pentane,  $-30^\circ\text{C}$ . c)  $[\text{KOTBu}]$ , THF, 25 °C. 2. THF, 25 °C (low yield due to incomplete crystallization).

the volatile by-products  $(\text{Me}_3\text{Si})_2\text{CH}_2$  or  $t\text{BuOSiMe}_3$  were readily removed under reduced pressure. Alternatively, ligand exchange from isolated THF adducts  $[(\text{thf})_x\text{MSiPh}_3]$  ( $\text{M} = \text{Li}$ ,  $\text{K} - \text{Cs}$ ) with **L** also gave complexes **1** and **3–5**.

The triphenylsilylanide complexes **1–5** were isolated in good yields from THF/*n*-pentane at  $-30^\circ\text{C}$ . They are insoluble in aliphatic hydrocarbons, slightly soluble in benzene, but well soluble in THF; they were characterized by elemental analysis, NMR spectroscopy, and single-crystal X-ray diffraction. The solubility and stability of the light yellow compounds in THF decreased at room temperature from  $\text{Li}$  ( $t_{1/2} > 14 \text{ d}$ ) to  $\text{Cs}$  ( $t_{1/2} \approx 12 \text{ h}$ ). The potassium complex also crystallized from neat THF as the solvate  $[(\text{L})(\text{thf})\text{KSiPh}_3]$  (**[THF]-3**) that gave amorphous  $[(\text{L})\text{KSiPh}_3]$  (**3**) under reduced pressure or extended storage at  $-30^\circ\text{C}$ , suggesting labile THF solvation. The  $^1\text{H}$  NMR spectra of compounds **1–5** in  $[\text{D}_8]\text{THF}$  show a sharp singlet

[a] D. Schuhknecht, Dr. V. Leich, Dr. T. P. Spaniol, Prof. Dr. J. Okuda  
Institute of Inorganic Chemistry, RWTH Aachen University  
Landoltweg 1, 52074 Aachen (Germany)  
E-mail: jun.okuda@ac.rwth-aachen.de

[b] I. Douair, Prof. Dr. L. Maron  
CNRS, INSA, UPS, UMR 5215, LPCNO  
Université de Toulouse 135 avenue de Rangueil  
31077 Toulouse (France)

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around  $\delta = 2.2$  ppm for the ligand methyl groups and resonances for the  $[\text{SiPh}_3]^-$  anion in the aromatic region with expected integral ratios. Although complexes **1** and **2** show two multiplets between  $\delta = 2.2$  and 2.7 ppm for the methylene protons of the ligand, **3–5** containing the larger cations display a broad resonance at  $\delta = 2.4$  ppm, indicating higher dynamics of the ligand ethylene bridges (Figure 1).<sup>[11]</sup> Partial ligand dissociation

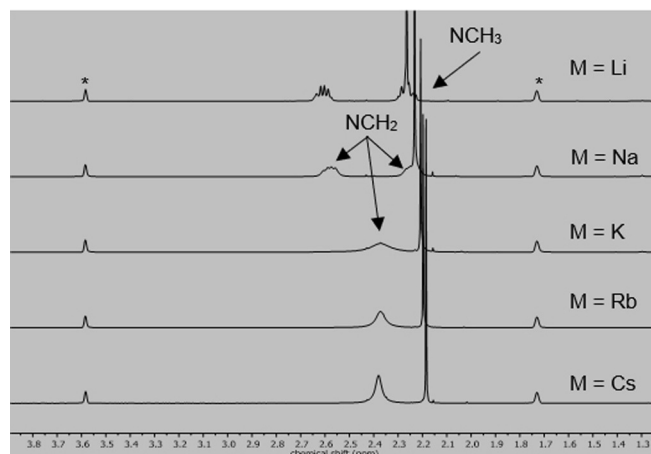


Figure 1.  $^1\text{H}$  NMR spectra of complexes **1–5** in  $[\text{D}_3]\text{THF}$  (\*) at  $25^\circ\text{C}$ .

due to larger ionic radii might also contribute to signal shift comparable to the free ligand.<sup>[8e]</sup>

Single crystals of the triphenylsilanides **1–5** were grown from THF/*n*-pentane at  $-30^\circ\text{C}$  or in case of **[THF]-3** from neat THF at room temperature. The smaller Li and Na complexes **1** and **2** crystallized in the acentric space group *Cc* with very similar lattice and structural parameters. Both cations show a distorted square pyramidal geometry (CN 5) with a  $\kappa^4$ -coordinated ligand, as well as a silicon-bonded  $[\text{SiPh}_3]^-$  anion (Figure 2a). The M–Si distances of 2.796(6) Å (**1**) and 2.9501(10) Å (**2**) are well in the range of other light alkali metal silanides (Table 1).<sup>[8b]</sup> In both structures, one of the silanide phenyl groups is bent ( $\text{Si}-\text{C}_i-\text{C}_o-\text{C}_m \approx 170^\circ$ , see the Supporting Information) due to Pauli repulsion, as was described for similar lithio-

Table 1. Selected structural parameters of the complexes **1–5** and **[THF]-3**.

Complex (M)	Ionic radius <sup>[16]</sup> [Å]/[CN]	$\text{O} \text{N}-\text{M}$ [Å]	M–Si [Å]	$\text{O} \text{M}-\text{C}_{\text{ph}}$ [Å]	$ \text{Si}-\text{C}_i-\text{C}_o-\text{C}_m $ [°]
<b>1</b> (Li)	0.76/(5)	2.26	2.793(9)	–	169.4
<b>2</b> (Na)	1.00/(5)	2.48	2.9501(10)	–	169.6
<b>[THF]-3</b> (K)	1.38/(6)	2.84	3.4328(11)	–	172.1
<b>3</b> (K)	1.46/(7)	2.80	(3.9180(12))	3.21	168.5
<b>4</b> (Rb)	1.61/(8)	3.04	3.775(2)	3.58	169.7
<b>5</b> (Cs)	1.74/(8)	3.16	(3.859(2))	3.66	173.8

silanides.<sup>[12]</sup> Potassium complex **[THF]-3** shows a capped trigonal prismatic geometry (CN 6) with additional THF coordination and a significantly longer K–Si distance (3.4328(11) Å) due to higher CN and a larger ionic radius (see the Supporting Information). In contrast, the structure of unsolvated **3** (Figure 2b) contains a non-bonding  $\text{K} \cdots \text{Si}$  interaction (3.9180(12) Å), but strong  $\text{K}-\eta^6$ -arene coordination (average  $\text{K}-\text{C}_{\text{ph}} \approx 3.21$  Å), as was previously observed in the complex  $[(\text{Me}_6\text{TREN})\text{KSiPh}_3]$ .<sup>[10,13]</sup> A switch from  $\eta^1$ - $\text{CH}_2$  to  $\eta^6$ -aryl coordination depending on the cation has been commonly observed in alkali metal benzyl complexes.<sup>[14]</sup> The heavier Rb and Cs complexes **4** and **5** show a more extended coordination sphere in the solid state: **4** crystallizes as dimer with bridging  $[\text{SiPh}_3]^-$  units (Figure 2c) similar to  $[(\text{thf})\text{MSiPh}_2\text{Bu}_2]_2$  ( $\text{M} = \text{Na}, \text{K}$ ),<sup>[15]</sup> although **5** shows a one-dimensional chain-like structure (see the Supporting Information) with inverted triphenylsilanide anions coordinating only through  $\text{Cs}-\text{C}_{\text{ph}}$  interactions ( $\text{O} \text{Cs}-\text{C}_{\text{ph}} \approx 3.66$  Å).

Similar to the  $\text{Me}_6\text{TREN}$  stabilized triphenylsilanide  $[(\text{Me}_6\text{TREN})\text{KSiPh}_3]$ ,<sup>[10]</sup> solutions of **1–5** in THF were pressurized with  $\text{H}_2$  (1 bar). Initial formation of the intermediate  $[\text{SiHPh}_2]^-$  and  $[\text{SiH}_2\text{Ph}]^-$ , as well as benzene as by-product, was observed after one and two days, respectively.<sup>[10,17]</sup> After seven days, the trihydrosilanide complexes  $[(\text{L})\text{MSiH}_3]_n$  **6–9** ( $\text{M} = \text{Li}-\text{Rb}$ ) were formed. Cesium complex **5** also reacted with  $\text{H}_2$  in a stepwise fashion to form the trihydrosilanide and benzene, but free ligand **L** and precipitation of colorless  $[\text{CsSiH}_3]_\infty$  was observed after five days (Scheme 2).

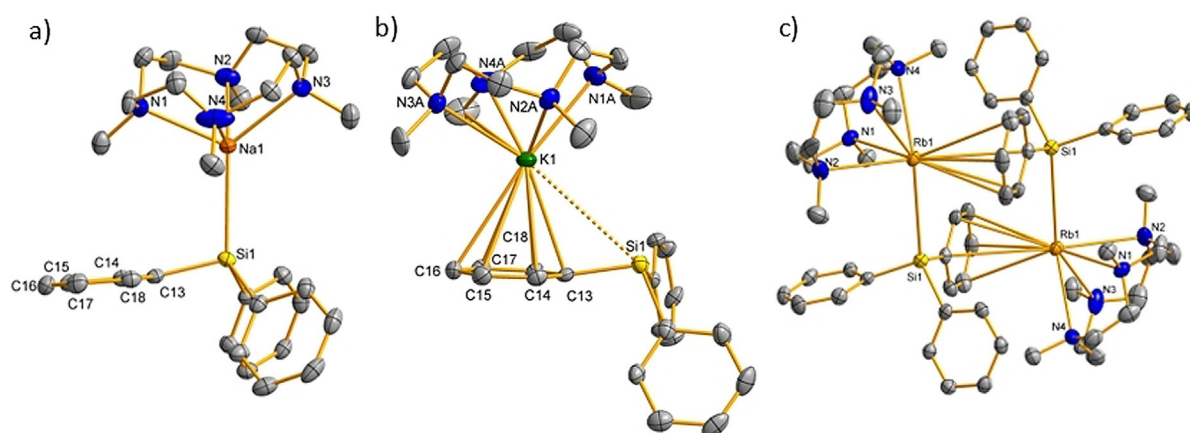
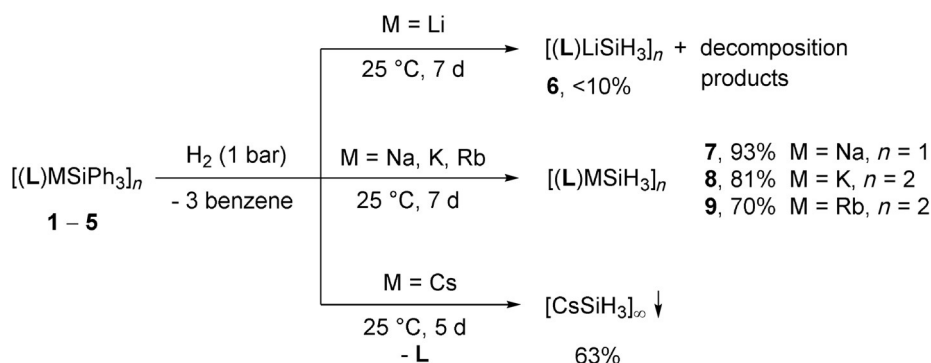
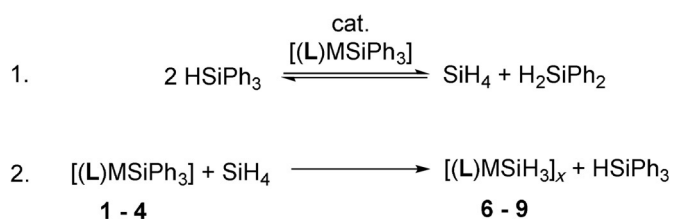


Figure 2. Molecular structures of a)  $[(\text{L})\text{NaSiPh}_3]$  (**2**), b)  $[(\text{L})\text{KSiPh}_3]$  (**3**) and c)  $[(\text{L})\text{RbSiPh}_3]_2$  (**4**). Displacement parameters are shown at a 50% probability level. Hydrogen atoms are omitted for clarity.



Scheme 2. Synthesis of trihydridosilanides 6–9 by hydrogenolysis.

The selectivity of the hydrogenolysis of **1** was low and crystallization from THF/*n*-pentane gave only low yield ( $\approx 10\%$ ) of **6**. Other reaction products included neutral silanes  $\text{H}_{x+1}\text{SiPh}_{3-x}$  ( $x=0-3$ ) and decomposed ligand fragments, as was observed in the  $^1\text{H}$  NMR spectrum (see the Supporting Information). Highly reactive lithium bases have been shown to degrade amines in several ways.<sup>[12b,18]</sup> In contrast, the heavier complexes  $[(\text{L})\text{MSiH}_3]_n$  ( $\text{M} = \text{Na}$ , **7**;  $\text{K}$ , **8**;  $\text{Rb}$ , **9**) were formed selectively and isolated from THF/*n*-pentane in good yield. Alternatively, the triphenylsilanides reacted with excess  $\text{PhSiH}_3$  to give complexes **6–9** after five minutes. The isolated yield for **6** was much higher (60%), and no decomposition of the ligand was observed.  $^1\text{H}$  NMR spectroscopy revealed immediate scrambling of  $\text{PhSiH}_3$  to form  $\text{Ph}_2\text{SiH}_2$  and  $\text{SiH}_4$  commonly observed catalyzed by strong bases (Scheme 3).<sup>[11c,19]</sup> Consecutive reaction of the in situ formed  $\text{SiH}_4$  and the triphenylsilanides **1–4** gave the  $[\text{SiH}_3]^-$  complexes through silane–silanide exchange.<sup>[20]</sup> Although complexes **7–9** are stable for weeks in solution and the solid state, complex **6** was significantly less stable ( $t_{1/2} \approx 2$  d).



Scheme 3. Reaction of complex 1–4 with  $\text{PhSiH}_3$ .

Complexes **6–9** are insoluble in aliphatic and aromatic hydrocarbons, but slightly soluble in THF. They were analyzed by elemental analysis, NMR spectroscopy and for **7–9** by X-ray diffraction. In  $[\text{D}_8]\text{THF}$ , they showed signals for the methyl and methylene protons of the ligand with chemical shift, integral ratio and shape comparable to the respective triphenylsilanide complexes **1–4**. Each complex showed a sharp singlet in the area of  $\delta = 1.25-1.41$  ppm with  $^{29}\text{Si}$  satellites ( $^1J_{\text{SiH}} \approx 75$  Hz) for the silanide anion  $[\text{SiH}_3]^-$ .<sup>[4b,21]</sup> A resonance between  $\delta = -160$  and  $-172$  ppm in the  $^{29}\text{Si}\{^1\text{H}\}$  NMR spectrum, as well as cross-

peaks in the  $^1\text{H}-^{29}\text{Si}\{^1\text{H}\}$  HSQC experiment further corroborated their formation.<sup>[22]</sup> Unlike the more labile bounded  $\text{Me}_6\text{TREN}$ , no dissociation of the macrocyclic  $\text{Me}_4\text{TACD}$  ligand was observed during synthesis and isolation of **6–9**.<sup>[23]</sup>

Single crystals of **7–9** suitable for X-ray analysis were grown from THF/benzene at  $25^\circ\text{C}$ . The highly reactive sodium complex  $[(\text{L})\text{NaSiH}_3]$  (**7**) crystallized as monomer with square pyramidal coordination geometry similar to the parent compound **2** (see the Supporting Information).<sup>[7]</sup> Several batches of crystals gave reproducibly low diffracting crystals, which prevented locating the hydrides in a Fourier difference map and assignment of the  $\kappa\text{Si}$  or  $\kappa^3\text{H}$  coordination mode due to similar expected  $\text{M}-\text{Si}$  distances.<sup>[7]</sup> The heavier silanides  $[(\text{L})\text{M}(\mu\text{-SiH}_3)]_2$  ( $\text{M} = \text{K}$  (**8**);  $\text{Rb}$  (**9**)) crystallized as dimers in the tetragonal space group  $P4_2/mnm$  with nearly identical lattice and structural parameters. The interatomic  $\text{K1}\cdots\text{K1}$  and  $\text{K1}\cdots\text{Si1}$  distances in **8** are comparable to those in the  $\beta\text{-KSiH}_3$  phase.<sup>[24]</sup> The hydrides were located in a Fourier difference map and refined. The  $\text{Si}-\text{H}$  and  $\text{K}-\text{H}$  interactions are comparable to those in the crown ether adduct,<sup>[24-25]</sup> but should be treated with care due to the heavy metals (Figure 3).

The structures of **7** and **8** were further investigated by DFT calculations (B3PW91). In both cases, the optimized structures

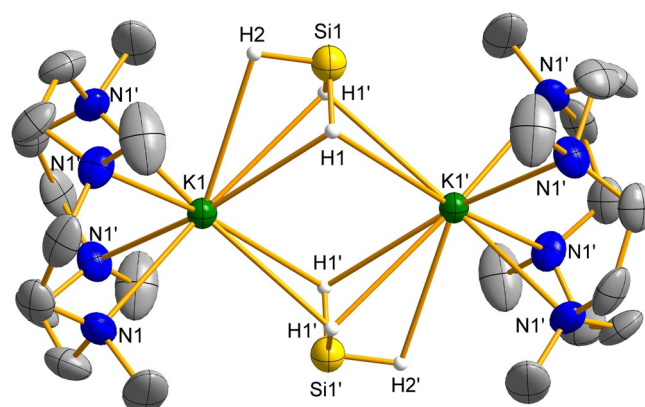


Figure 3. Molecular structure of  $[(\text{L})\text{KSih}_3]_2$  (**8**). Displacement parameters are shown at a 50% probability level. Hydrogen atoms and solvent in the lattice are omitted for clarity. Selected interatomic distances [ $\text{\AA}$ ]:  $\text{K1}-\text{N1}$  2.862(2),  $\text{K1}\cdots\text{K1}'$  4.4691(17),  $\text{K1}\cdots\text{Si1}$  3.5625(13),  $\text{K1}-\text{H1}$  3.06(2),  $\text{K1}-\text{H2}$  3.12(7),  $\text{Si1}-\text{H1}$  1.31(3),  $\text{Si1}-\text{H2}$  1.32(7).

compare well with the ones observed in the solid state (see the Supporting Information). Two possible structures of **7** were optimized with a low energy difference of approximately 2 kcal mol<sup>-1</sup> in favor of the  $\kappa$ Si-bonded [SiH<sub>3</sub>]<sup>-</sup> group. For both structures, natural bonding analysis (NBO) was carried out. For the most stable complex, the Na–Si Wiberg bond index (WBI) is 0.45 indicating a polar covalent Na–Si bond. The second isomer contains an inverted hydride-bridged [ $\kappa^3$ H-SiH<sub>3</sub>]<sup>-</sup> ligand with a significantly lower Na–Si WBI (0.12), in line with a weaker Na–Si interaction. The stability of the latter is therefore explained by the second-order donor–acceptor interaction, in which strong donations of approximately 43 kcal mol<sup>-1</sup> from the covalent Si–H bonds (WBI 0.86) to the sodium cation are found. As was observed in the solid state for [ $\alpha$ -MSiH<sub>3</sub>]<sub>scr</sub>, both structures might be present and interchangeable, preventing location of the hydrides in the crystal structure.<sup>[4b,24]</sup> In contrast, the dimeric potassium complex **8** is significantly more stable with bridging [ $\kappa^3$ H-SiH<sub>3</sub>] units (23.3 kcal mol<sup>-1</sup>). For the dimer, the Si–K WBI is expectedly low (0.06). For the inverted hydride-bridged isomer of **7**, donations from the covalent Si–H bonds (WBI 0.89) towards the cations (about 22 kcal mol<sup>-1</sup> each) ensure the stabilization of the complex.

In conclusion, the macrocyclic ligand Me<sub>4</sub>TACD stabilizes the full range of alkali metal triphenylsilanides that show the structural trend from Si coordination in **1** and **2** towards M...C<sub>ph</sub> interactions in the heavier analogues **4** and **5**. Both coordination modes were observed in the potassium complexes **3** and [THF]-**3** depending on the crystallization conditions. The [(L)MSiPh<sub>3</sub>] complexes reacted with H<sub>2</sub> in THF at ambient conditions to give trihydridosilanides [(L)MSiH<sub>3</sub>]<sub>x</sub> and benzene. Both Na and K complexes showed an ionic structure with Si–H donation towards the metal center. In the case of Li, strong basicity hindered the selective formation by hydrogenolysis, however, silane–silanide exchange from in situ formed SiH<sub>4</sub> gave the lightest silanide [(L)LiSiH<sub>3</sub>] in moderate yield. As was observed for early main-group metal hydrides,<sup>[26]</sup> smaller aggregates could show improved dehydrogenation kinetics, which will be further investigated.

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## Conflict of interest

The authors declare no conflict of interest.

**Keywords:** alkali metals · hydrogen storage · macrocyclic ligands · metal hydrides · silanides

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