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Crown ether adducts of light alkali metal triphenylsilyls: synthesis, structure and hydrosilylation catalysis*

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Alkali metal triphenylsilyls [Li(12-crown-4)SiPh₃]·(thf)_{0.5} (2), [Na(15-crown-5)SiPh₃]·(thf)_{0.5} (3) and [K(18crown-6)SiPh₃(thf)] (4) were synthesized using 1,1,1-trimethyl-2,2,2-triphenyldisilane (Ph₃SiSiMe₃) and isolated in high yields. Solid state structures were determined by single crystal X-ray diffraction. These alkali metal silvls catalyzed the regioselective hydrosilvlation of 1,1-diphenylethylene to give the anti-Markovnikov product. The presence of crown ethers enhanced the reactivity of the metal silyls in hydrosilylation catalysis

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Introduction

Organosilicon compounds are valuable intermediates of considerable interest in materials science.¹ Applications in synthetic chemistry include their use as protecting groups in organic chemistry and for regio- and stereoselective C-C bond formation under mild conditions.² Prominent examples of organosilicon mediated reactions are the Sakurai reaction,³ the Mukaiyama aldol reaction,⁴ Peterson olefination⁵ and Hiyama cross coupling.⁶ Reactivity studies of organometallic silicon compounds provided insight into the mechanisms of these reactions. Therefore isolation and full characterization of organometallic silicon compounds help to understand the nature of the metal-silicon bond. In this regard alkali metal silyls could serve as precursors for transition metal silyls or model complexes itself.

The synthesis of alkali metal silvls often requires specific silanes as starting materials limiting their general application. Reproducible protocols to produce these metal silvls in high yields from commercially available chemicals could benefit their application. Procedures reported in the literature are compiled in Scheme 1.

The cleavage of a symmetrical disilane, which contains one or more aryl groups on the silicon, with alkali metals is the most common method to prepare metal silvls (Scheme 1a). The increase in reactivity from lithium to cesium comes along with the decrease in the solubility of the alkali metal silyls.

a) RSiSiR
$$\xrightarrow{2 \text{ M}}$$
 2 MSiR $\stackrel{M = \text{Li}, \text{Na}, \text{K}; \text{R} = \text{Ph}_3, \text{Ph}_2\text{Me}, \text{PhMe}_2, \text{Ph}_2^t\text{Bu}, \text{PhH}_2, \text{Ph}_2\text{H}$
b) R_3SiSiR'_3 $\xrightarrow{\text{MOR}''}_{-\text{R}'_3SiOR''}$ MSiR₃ $\stackrel{M = \text{Na}, \text{K}; \text{R}'' = \text{Me}; \text{R} = \text{R}' = \text{Me}}_{\text{M} = \text{K}; \text{R}'' = t\text{Bu}; \text{R} = \text{R}' = \text{Ph}, \text{Me}}_{\text{or R} = \text{Ph}, \text{R}' = t\text{Bu}; \text{R} = \text{R}' = \text{Ph}, \text{Me}}_{\text{or R} = \text{Ph}, \text{R}' = \text{Me}}$
c) R_3SiH $\xrightarrow{\begin{pmatrix}-1/2 \text{ H}_2\\ \text{MH}\\ -\text{H}_2\end{pmatrix}}$ MSiR₃ $\stackrel{M = \text{Li}; \text{R} = \text{GePh}_3, \text{Ph}}_{\text{M} = \text{K}; \text{R} = \text{Ph}, \text{Et}}$
d) M_n[Si(SiMe_3)_{4-n}]_{1+n} $\xrightarrow{\text{M'R}_{1-n}}_{\text{M} = \text{K}; \text{R} = \text{O'Bu}}_{\text{SiMe}_3}$

Scheme 1 Syntheses of alkali metal silvls reported in the literature.

Examples are $[MSiPh_3]$ (M = Li, Na, K),⁷ $[LiSiPh_2Me]$,⁸ [LiSiPhMe₂],⁸ [KSiPh₂^tBu],⁹ [KSiPh₂H]¹⁰ and [KSiPhH₂].¹¹ The cleavage of symmetrical or unsymmetrical disilanes with alkali metal alkoxides (Scheme 1b) was used to synthesize [MSiMe₃] $(M = Na, K)^{12}$ and $[KSiR_3] (R_3 = Me_3, Ph_2Me, Ph_3).^{12c}$ The use of HMPA, DMI or DMPU as solvents limited the application of these procedures. The reaction of a silane with an alkali metal or alkali metal hydride under dihydrogen release was reported only for a few compounds (Scheme 1c). Examples are [LiSi- $(GePh_3)_3$],¹³ [LiSiPh₃],^{7b} [KSiR₃] (R₃ = Et₃, Ph₃)¹⁴ and [MSiH₃] (M = K, Rb, Cs).¹⁵ This straightforward strategy is hampered by low yields, side reactions and the preparation of highly activated alkali metals. Alkali metal "hypersilyls" [MSi(SiMe₃)₃] (M = Li-Cs) have attracted some interest due to their stability, simple and high yield syntheses.¹⁶ They can be prepared from

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Institute of Inorganic Chemistry, RWTH Aachen University, Landoltweg 1, D-52056 Aachen, Germany. E-mail: jun.okuda@ac.rwth-aachen.de; Fax: +49 241 80 92 644 †Electronic supplementary information (ESI) available: NMR spectra, X-ray crystallographic details and data. CCDC 993779 (2β), 993780 (3β) and 993781 (4). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c4dt00916a

 $Si(SiMe_3)_4$ and common alkali metal reagents¹⁷ or by transmetalation¹⁸ (Scheme 1d).

In many cases the metal silyls were not isolated and characterized fully due to their high reactivity towards water and oxygen. Reactivity studies or applications in catalysis of alkali metal silyls remain still scarce. We report here the synthesis, characterization and application in catalytic hydrosilylation of $[Li(12-crown-4)SiPh_3]\cdot(thf)_{0.5}$ (2), $[Na(15-crown-5)SiPh_3]\cdot(thf)_{0.5}$ (3) and $[K(18-crown-6)SiPh_3(thf)]$ (4).

Results and discussion

Synthesis and isolation of alkali metal silyls

All metal silyls were synthesized from 1,1,1-trimethyl-2,2,2-triphenyldisilane^{7d} **1** as a starting material. The use of disilane **1** offers some advantage over established preparation methods: (1) 1,1,1-trimethyl-2,2,2-triphenyldisilane can be prepared from commercially available chemicals in high yield and purity; (2) nucleophilic attack at the SiMe₃- is favored over the SiPh₃-silicon center, thus giving one silyl species selectively; (3) the coupling products $CH_2(SiMe_3)_2$ and ${}^{t}BuOSiMe_3$ are low boiling, stable compounds, which suppress the back reaction to the starting materials.

In all cases the procedures were simple. To a solution of **1** a solution of the appropriate nucleophile/crown ether was added slowly and stirred for 1–12 h. After the time indicated the product crystallized from THF-hexane solution. [Li(12-crown-4)SiPh₃]·(thf)_{0.5} (2) was prepared from lithium alkyl LiCH₂-SiMe₃/12-crown-4 in 80% yield (Scheme 2). In the case of **2** only a slight increase in yield compared to [LiSiPh₃(thf)]¹⁹ (63%) was achieved. Common lithium reagents such as lithium methyl, *n*-butyl and *tert*-butoxide were not able to cleave **1** selectively. Addition of 12-crown-4 to the reaction solution reduced the reaction time from 24 h to 12 h.

 $[Na(15\text{-}crown-5)SiPh_3]\cdot(thf)_{0.5}$ (3) was synthesized in quantitative yield starting from disilane 1 and sodium *tert*-butoxide/ 15-crown-5 within 2 h (Scheme 2). Without addition of crown ether no conversion to the sodium silyl was observed. Sodium triphenylsilyl $[NaSiPh_3]^{20}$ was synthesized before by cleavage of

	I	LiCH ₂ SiMe ₃ , 12 h 12-crown-4 – CH ₂ (SiMe ₃) ₂	[Li(12-crown-4)SiPh ₃]-(thf) _{0.5} 2 80%
Ph ₃ SiSiMe ₃ · 1	1.THF, 25 °C 2. THF/hexane -30 °C	NaO ^{<i>t</i>} Bu, 2 h 15-crown-5 – ^t BuOSiMe ₃	[Na(15-crown-5)SiPh ₃] (th f) _{0.5} 3 , 99%
		KO ^t Bu, 1 h <u>18-crown-6</u> − ^t BuOSiMe ₃	[K(18-crown-6)SiPh ₃ (thf)] 4 , 99%

Scheme 2 Synthesis of crown ether adducts of Li/Na/K-triphenylsilyls.

hexaphenyldisilane with sodium metal in 71% yield. To the best of our knowledge, it was never isolated or characterized.

[K(18-crown-6)SiPh₃(thf)] (4) was synthesized reacting disilane **1** with potassium *tert*-butoxide/18-crown-6²¹ in THF for 1 h following a modified procedure.^{12c} Potassium silyl 4 was isolated in quantitative yield (99%) as analytically pure orange powder (Scheme 2). Recently published synthesis of [K(18crown-6)SiPh₃]²² reported a yield of 88% (16 h) and 75% for [KSiPh₃].²³

Characterization of alkali metal silyls

¹H NMR spectra of **2**, **3** and **4** in d₈-THF displayed one singlet at $\delta \sim 3.5$ ppm for the crown ether methylene protons and three multiplets at $\delta \sim 6.8$ -7.4 ppm for the *para-*, *meta-* and *ortho-*Ph protons of the phenyl substituents (see ESI†). ¹³C{¹H} and ²⁹Si{¹H} NMR data are listed in Table 1 and are comparable to the data published for [LiSiPh₃] and [KSiPh₃].²⁴

The metal cation and complexation with crown ethers has only a small influence on the 13 C NMR shifts of the *ortho*-, *meta-* and *para-*Ph carbons. Going from Li to K, a small downfield shift of the *ipso* carbon atom from 156.30 ppm to 160.95 ppm was observed.

It was stated before that the NMR data are consistent with a strong M–Si interaction with covalent character, forming monomeric metal silyl species in ethereal solvents.²⁴ Recently, DFT calculations indicated a highly polar localized Ca–Si bond in $[Ca(SiPh_3)_2(thf)_4]$.²⁵ The solution structure of **2**, **3** and **4** appears to be similar to that of alkali metal silyls [MSiPh₃] (M = Li and K).

Crystals of 2, 3 and 4 were grown from THF-hexane at -30 °C. X-ray diffraction at low temperature for compounds 2 and 3 resulted only in low resolution data that could not be indexed with only one unit cell. Heating the crystals to 220 K revealed a reversible solid state phase transition. Data collections were performed at 100 K and 220 K.

Evaluation of the low temperature data of $[\text{Li}(12\text{-crown-4})\text{-}SiPh_3]\cdot(thf)_{0.5}$ (2 α) did not allow satisfactory indexing of the unit cell. Weak diffraction power and twinning with several independent domains suggest a unit cell of approximately 7808 Å³ with trigonal metrics. The high temperature data (2 β) allowed for a structure solution in the trigonal space group $P\bar{3}c1$ with a unit cell four times smaller than the low temperature phase. Despite the low diffraction power, a restrained but satisfactory structure model was obtained. [Li(12-crown-4)-SiPh_3] units cocrystallized with 0.5 equivalents of the solvate thf in agreement with the ¹H NMR spectrum.

Table 1	¹³ C{ ¹ H} and ²⁹ S	{ ¹ H} NMR data	a of 2 , 3 and 4 in ppm ^a	
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	ipso	ortho	meta	para	²⁹ Si{ ¹ H}
2	156.30	137.11	126.96	124.61	-8.60
3	157.70	137.30	126.72	124.13	-6.60
4	160.95	137.20	126.46	123.10	-8.24

^{*a*} NMR spectra were recorded at 25 °C in d₈-THF solutions.



Fig. 1 Ball and stick model of the main residue of 2β . Hydrogen atoms and solvent molecules are omitted for clarity. Selected bond lengths [Å] and angles [°]: Li1–Si1 2.650(9), Li1–O1–4_{avg} 2.11(1), Si1–C9 1.923(5), Li1–Si1–C9 116.43(9), Si1–Li1–O1 118.9(3), Si1–Li1–O2 113.8(3), Si1–Li1–O3 112.4(3), Si1–Li1–O4 115.0(2).

Li is enclosed in a distorted square pyramidal geometry with the crown ether occupying the square plane (Fig. 1). The Li–Si contact is located along a 3-fold axis resulting in a heavily disordered structure model for the C_4 symmetric crown ether. The 3-fold rotation axis of the silyl group is compatible with the crystal symmetry. The Li1–Si1 bond length of 2.650(9) Å and Si1–Li1–O1–4 angles from 112.4(3)° to 118.9(3)° indicate a similar interaction between lithium and the silyl anion as in literature known compounds ([[LiSiMe_3]₂(TMEDA)₃] = 2.70(1) Å,²⁶ [Li(thf)₃Si^fBuPh₂] = 2.675(5) Å,²⁷ [Li(thf)₃SiPh₃] = 2.672(13) Å,¹⁹ [Li(thf)₃Si(SiMe_3)₃] = 2.672 Å,²⁸ [Li(thf)₃Si(SiMe_3)₃]₂ = 2.689(4)²⁹). Crystal data and refinement results for all structures are given in Table 3; details of the low temperature phase 2α are given in the ESI.†

Low temperature diffraction data of $[Na(15\text{-}crown-5)\text{-}SiPh_3]\cdot(thf)_{0.5}$ (3 α) were of slightly better intensity and could be indexed as twin with at least three components in a nearly trigonal unit cell (a = 25.313(15) Å, b = 25.329(15) Å, c = 10.576(7)Å, $\alpha = 89.673(14)^\circ$, $\beta = 90.506(15)^\circ$, $\gamma = 117.638(13)^\circ$) with pseudo translation symmetry along the *a*-axis. A structure solution was obtained in $P\bar{1}$ and the basic connectivity of the molecule could be derived using an isotropic model with an average Na–Si distance of 2.99(1) Å.

The high temperature phase 3β crystallizes in $P\bar{3}$ and is similar to 2β with respect to connectivity and packing. The lower crystal symmetry is compensated by a smaller unit cell, resulting in a closely related asymmetric unit when compared to 2β , including 0.5 equivalents of cocrystallized thf. The Na– Si contact extends along the 3-fold axis with a bond length of 2.983(4) Å, which is comparable to known sodium silyl radical ([NaSi(Si^tBu₂Me)₂] = 3.0744(8) Å³⁰) or silyls [NaSi(SiMe₃)₃]₂ = 3.049(1) Å,^{18a} [NaSi^tBu₃]₂ = 3.073(4) Å,³¹ [Na(thf)₂Si^tBu₃]₂ = 2.919(1) Å,³¹ [Na(PMDTA)Si^tBu₃] = 2.967(2) Å,³¹ [NaSi^tBu₂Ph]₂ = 2.8811(19) Å,³² [Na(thf)Si^tBu₂Ph] = 2.9910(2) Å³³). A distorted pentagonal pyramidal coordination is found for the sodium cation (Fig. 2). The tip is occupied by the ordered triphenylsilyl, the base is formed by the C_5 -symmetric crown ether, disordered over the three symmetry equivalent positions. The Si1–Na1–O1–5 angles range from 99.9(3)° to 124.8(3)° but have to be interpreted with care as the structure model is based on a heavily restrained and constructed model that barely included the assignment of electron density maxima in Fourier maps.

[K(18-crown-6)SiPh₃(thf)] (4) crystallizes in the monoclinic space group *Cc* with *Z* = 4. The molecular connectivity differs from that in Li and Na analogues by an extended coordination sphere. The larger size of the potassium cation allows the coordination of one thf molecule (K1–O7 = 2.810(5) Å) (Fig. 3).



Fig. 2 Ball and stick model of the main residue of 3β . Hydrogen atoms and solvent molecules are omitted for clarity. Selected bond lengths [Å] and angles [°]: Na1–Si1 2.983(4), Na1–O1–5avg 2.53(1), Si1–C21 915(6), Si1–Na1–O1 105.9(3), Si1–Na1–O2 117.7(3), Si1–Na1–O3 99.9(3), Si1–Na1–O4 124.8(3), Si1–Na1–O5 112.9(3).



Fig. 3 Ball and stick model of the asymmetric unit of **4**. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: K1–Si1 3.460(3), K1–O7 2.810(5), K1–O1– 6_{avg} 2.819(5), Si1–K1–O7 172.75(11), Si1–K1–O1– 6_{avg} 94.75(12), K1–Si1–C10 118.3(2), K1–Si1–C11 111.9(2), K1–Si1–C12 124.1(2).

A K1–Si1 bond length of 3.460(3) Å and an average Si1–K1–O1–6 angle of 94.75(12)° (measured at 100(2) K) suggest a stronger interaction between potassium cation and the silyl anion compared to $[K(18\text{-}crown-6)\text{SiPh}_3]^{22,34}$ (K–Si = 3.5404(5) Å at 100(2) K). In this compound, $[K(18\text{-}crown-6)\text{SiPh}_3]$ units are connected by intermolecular π -interactions between a potassium atom and one of the phenyl rings of the silyl anion to form chains. In 4 the thf ligand disrupts these chains to form monomeric units in the solid state. This results in higher nucleophilicity of the triphenylsilyl anion in solution.

Catalytic hydrosilylation with alkali metal silyls

The alkali metal silyls **2**, **3** and **4** were tested in the catalytic hydrosilylation of 1,1-diphenylethylene (1,1-DPE) and their activity compared to that of known metal silyls (Table 2). Using potassium silyl $[KSiPh_3(thf)]^{25}$ (2.5 mol% catalyst loading) quantitative hydrosilylation of 1,1-DPE was observed at 40, 60 and 80 °C within 174, 83 and 39 h, without any catalyst deactivation (Table 2, entries 1–3).

Use of diphenylsilane (H₂SiPh₂) and phenylsilane (H₃SiPh) shortened reaction times, but the yield of the product decreased to 87 and 78%, respectively (Table 2, entries 4–5). Interestingly, known [LiSiPh₃(thf)₃]¹⁹ also catalyzed the hydrosilylation of 1,1-DPE within 40 h at 80 °C to give the product in 96% yield (Table 2, entry 6). The catalyst is deactivated after this time. Using alkali metal silyls **2**, **3** and **4** in the catalytic hydrosilylation shortened reaction times without catalyst deactivation (Table 2, entries 9–11). In all cases quantitative conversion was observed at 80 °C after 15–20 h. Alkali metal triphenylsilyls synthesized by established methods showed comparable activities in the hydrosilylation of 1,1-DPE (Table 2, entries 7/8). Complexation of alkali metal with crown ethers increased both reactivity and stability of the resulting

Table 2 Hydrosilylation of 1,1-DPE with alkali metal silyls

	Ph + 1	2.5 mol %	Cat.	H L	SiR ₃
	Ph	d ₈ -TH	IF	Ph Ph	
Entry ^a	Silane	Cat.	$T [^{\circ}C]$	<i>t</i> [h]	Conversion ²
1	HSiPh ₃	[KSiPh ₃ (thf)] ²⁵	40	174	>99
2	$HSiPh_3$	[KSiPh ₃ (thf)] ²⁵	60	83	>99
3	HSiPh ₃	[KSiPh ₃ (thf)] ²⁵	80	39	>99
4	H_2SiPh_2	[KSiPh ₃ (thf)] ²⁵	80	2	87 ^c
5	H ₃ SiPh	[KSiPh ₃ (thf)] ²⁵	80	2	78^c
6	$HSiPh_3$	[LiSiPh ₃ (thf) ₃] ¹⁹	80	40	96 ^c
7	HSiPh ₃	$[LiSiPh_3(thf)_3]^{19} + 12$ -crown-4	80	16	>99
8	HSiPh ₃	[KSiPh ₃ (thf)] ²⁵ + 18-crown-6	80	20.5	>99
9	HSiPh ₃	2	80	15	>99
10	HSiPh ₃	3	80	18	>99
11	HSiPh ₃	4	80	20	>99

^{*a*} Reaction conditions: catalyst (2.5 μmol), alkene (0.1 mmol), silane (0.11 mmol). ^{*b*} Determined by ¹H NMR spectroscopy. ^{*c*} Catalyst deactivation after time indicated.

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Table 3 Crystal data and refinement results for 2β , 3β and 4

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Compound	2β	3β	4
Empirical	C ₂₈ H ₃₅ LiO _{4.5} Si	C ₃₀ H ₃₉ NaO _{5.5} Si	C ₃₄ H ₄₇ KO ₇ Si
iormula			694.99
$M(g \mod 1)$	4/8.59	538.69	634.90
Temperature (K)	220(2)	220(2)	100(2)
Crystal system	Trigonal	Trigonal	Monoclinic
Space group no.	P3c1 (165)	$P\bar{3}(147)$	Cc(9)
a (Å)	11.9898(9)	12.858(5)	19.801(6)
b (Å)	_	_	14.731(4)
c (Å)	21.5449(17)	10.756(5)	12.752(4)
$\beta(\circ)$	_ ()	_ ()	112.535(5)
$V(Å^3)$	2682.2(5)	1540.1(14)	3435.6(18)
Z	4	2	4
$\mu ({\rm mm}^{-1})$	0.120	0.126	0.234
Total/unique	30 183/1837	4593/1817	12 783/7033
reflections			
Variables refined	114	123	389
	(17 restraints)	(76 restraints)	(2 restraints)
Rint	0.0543	0.0308	0.0765
wR_2 (all/obs)	0.3126/0.2733	0.2141/0.1900	0.1944/0.1862
R_1 (all/obs)	0.1287/0.0961	0.1661/0.1155	0.0803/0.0715
$GOF \text{ on } F^2$	1.040	1.005	1.080
Diff_peak/hole	0.397/-0.403	0.450/-0.436	0 751/-0 469
$(e \ \Delta^{-3})$	0.00077 0.100	0.100/ 0.100	0.701/ 0.105
Elack parameter			0.00(0)
	002770	002780	0.00(9)
ULDU	332//3	333/00	999/01

metal silyls. Hydrosilylation of styrene, 1-octene and cyclohexene with 2, 3 and 4 as catalysts was not observed.

In comparison with hydrosilylation catalysts based on the alkaline earth metals ($[M(DMAT)_2(thf)_2]$ and [K(DMAT)], M = Ca, Sr, DMAT = CH(SiMe₃)C₆H₄-2-(NMe₂), reaction times: 2–24 h)³⁵ reaction times are longer for alkali metal silyls. Regioselectivity changed to give anti-Markovnikov hydrosilylation products. As proposed by Harder *et al.*, hydrosilylation catalyzed by metal silyls might operate through a different mechanism.^{35,36} A silyl migration mechanism, established for transition metal-catalyzed hydrosilylation,³⁷ could be feasible (Scheme 3). The first step of the catalytic cycle involves a fast insertion of an alkene into the metal silicon bond to give a resonance stabilized metal alkyl. This undergoes *rate-determining* σ -bond metathesis with a silane to regenerate the silyl and the hydrosilylated product.²⁵



Scheme 3 Proposed silyl migration mechanism.

Conclusions

In conclusion, a series of light alkali metal triphenylsilyls were synthesized from 1,1,1-trimethyl-2,2,2-triphenyldisilane (Ph₃Si-SiMe₃) and characterized by spectroscopic and X-ray diffraction methods. They catalyze the anti-Markovnikov hydrosilylation of activated olefins, supporting the active role of metal silyls in this type of catalysis. Thus coordination of alkali metal silyls with crown ethers enhances both stability and reactivity of the resulting complexes.

Experimental

General experimental remarks

All operations were performed under an inert atmosphere of dry argon using standard Schlenk line or glove box techniques. d8-THF was distilled under argon from sodium/benzophenone ketyl prior to use. 1,1-Diphenylethene and 1,4,7,10-tetraoxacyclododecane (12-crown-4) were dried over CaH2 and distilled under argon prior to use. Triphenylsilane, 1,4,7,10,13-pentaoxacyclopentadecane (15-crown-5) and 1,4,7,10,13,16-hexaoxacyclooctadecane (18-crown-6) were purified by vacuum sublimation. THF and pentane were purified using a MB SPS-800 solvent purification system. The metal content was determined by atom absorption spectroscopy (Shimadzu AA-6200, 460.7 nm, air/acetylene flame). NMR spectra were recorded on a Bruker Avance II 400 and a Bruker Avance III HD 400 spectrometer at 25 °C in J. Young type NMR tubes. Chemical shifts for ¹H, ¹³C{¹H} and ²⁹Si{¹H} NMR spectra were referenced internally using the residual solvent resonance and are reported relative to tetramethylsilane. ⁷Li{¹H} spectra were referenced to LiCl in D_2O (1 M). The resonances in ¹H and ¹³C NMR spectra were assigned on the basis of two-dimensional NMR experiments (COSY, HSQC, HMBC). 1,1,1-Trimethyl-2,2,2-triphenyldisilane^{7d} and $[LiCH_2SiMe_3]^{38}$ were prepared according to literature procedures.

Synthesis of [Li(12-crown-4)SiPh₃]-(thf)_{0.5} (2). A solution of [LiCH₂SiMe₃] (47 mg, 0.50 mmol) in THF (1 mL) was added to a solution of 1,1,1-trimethyl-2,2,2-triphenyldisilane (167 mg, 0.50 mmol) in THF (1 mL). The reaction mixture turned yellow and was stirred for 12 h at r.t. After 12 h 12-crown-4 (44 mg, 0.50 mmol) in THF (1 mL) was added and [Li(12-crown-4)SiPh₃]-(thf)_{0.5} precipitated from the reaction mixture. The solvent was removed under reduced pressure and the crude product was washed with pentane (3 × 3 mL). After drying under reduced pressure, [Li(12-crown-4)SiPh₃]-(thf)_{0.5} was obtained as pale yellow powder (193 mg, 0.40 mmol, 80%). Crystals of [Li(12-crown-4)SiPh₃]-(thf)_{0.5} suitable for single crystal X-ray analysis were grown from THF–hexane at -30 °C over a period of 24 h.

¹H NMR (d₈-THF, 400.1 MHz): δ 1.78 (m, 2H, thf), 3.61 (m, 2H, thf), 3.62 (s, 16H, 12-crown-4), 6.86–6.91 (m, 3H, *para*-Ph), 6.96–7.00 (m, 6H, *meta*-Ph), 7.33–7.36 (m, 6H, *ortho*-Ph). ¹³C-{¹H} NMR (d₈-THF, 100.6 MHz): δ 26.44 (thf), 68.28 (thf), 71.37

(12-crown-4), 124.61 (*para*-Ph), 126.96 (*meta*-Ph), 137.11 (*ortho*-Ph), 156.30 (*ipso*-Ph). ²⁹Si{¹H} NMR (d₈-THF, 25 °C, 79.5 MHz): δ –8.60 (LiS*i*). ⁷Li{¹H} NMR (d₈-THF, 155.5 MHz): δ 0.59 (s, *Li*(12-crown-4)Si). Anal. calc. for C₂₈H₃₅LiO_{4.5}Si (478.59 g mol⁻¹): C, 70.27, H, 7.37; Li, 1.45. Found: C, 69.37; H, 7.08; Li, 1.45%.

Synthesis of $[Na(15\text{-}crown\text{-}5)SiPh_3]$ ·(thf)_{0.5} (3). A solution of sodium *tert*-butoxide (96 mg, 1.00 mmol) in THF (2 mL) was added to a solution of 15-crown-5 (220 mg, 1.00 mmol) and 1,1,1-trimethyl-2,2,2-triphenyldisilane (333 mg, 1.00 mmol) in THF (2 mL). The reaction mixture turned yellow and was stirred for 2 h at r.t. The solvent was removed under reduced pressure and the crude product washed with pentane (3 × 3 mL). After drying under reduced pressure, $[Na(15\text{-}crown\text{-}5)SiPh_3]$ ·(thf)_{0.5} (538 mg, 0.99 mmol, 99%) was obtained as pale yellow powder. Crystals of $[Na(15\text{-}crown\text{-}5)SiPh_3]$ ·(thf)_{0.5} suitable for single crystal X-ray analysis were grown from THF–hexane at -30 °C over a period of 24 h.

¹H NMR (d₈-THF, 400.1 MHz): δ 1.78 (m, 2H, thf), 3.58 (s, 20H, 15-crown-5), 3.62 (m, 2H, thf), 6.82–6.86 (m, 3H, para-Ph), 6.93–6.97 (m, 6H, meta-Ph), 7.37–7.39 (m, 6H, ortho-Ph). ¹³C{¹H} NMR (d₈-THF, 100.6 MHz): δ 26.43 (thf), 68.26 (thf), 69.86 (15-crown-5), 124.13 (para-Ph), 126.72 (meta-Ph), 137.30 (ortho-Ph), 157.70 (ipso-Ph). ²⁹Si{¹H} NMR (d₈-THF, 25 °C, 79.5 MHz): δ –6.60 (NaSi). Anal. calc. for C₃₀H₃₉NaO_{5.5}Si (538.69 g mol⁻¹): Na, 4.27. Found: Na, 3.83%.

Synthesis of [K(18-crown-6)SiPh₃(thf)] (4). A solution of potassium *tert*-butoxide (112 mg, 1.00 mmol) in THF (1 mL) was added to a solution of 18-crown-6 (264 mg, 1.00 mmol) and 1,1,1-trimethyl-2,2,2-triphenyldisilane (333 mg, 1.00 mmol) in THF (2 mL). The reaction mixture immediately turned yellow/ orange and was stirred for 1 h at r.t. The solvent was removed under reduced pressure and the crude product was washed with pentane (3 × 3 mL). After drying under reduced pressure, [K(18-crown-6)SiPh₃(thf)] was obtained as yellow powder (634 mg, 1.00 mmol, 99%). Crystals of [K(18-crown-6)SiPh₃(thf)] suitable for single crystal X-ray analysis were grown from THF– hexane at -30 °C over a period of 12 h.

¹H NMR (d₈-THF, 400.1 MHz): δ 1.78 (m, 4H, thf), 3.52 (s, 24H, 18-crown-6), 3.62 (m, 4H, thf), 6.73–6.77 (m, 3H, para-Ph), 6.87–6.91 (m, 6H, meta-Ph), 7.36–7.39 (m, 6H, ortho-Ph). ¹³C{¹H} NMR (d₈-THF, 100.6 MHz): δ 23.26 (thf), 68.27 (thf), 71.09 (18-crown-6), 123.10 (para-Ph), 126.46 (meta-Ph), 137.20 (ortho-Ph), 160.95 (ipso-Ph). ²⁹Si{¹H} NMR (d₈-THF, 25 °C, 79.5 MHz): $\delta = 8.24$ (KSi). Anal. calc. for C₃₄H₄₇KO₇Si (634.90 g mol⁻¹): K, 6.16. Found: K, 6.12%.

Hydrosilylation of 1,1-diphenylethene

Hydrosilylation experiments were performed as follows: a solution of catalyst (2.5 μ mol) in d₈-THF (0.5 mL) in a Young's NMR tube was treated with 1,1-DPE (0.10 mmol). Immediately the reaction mixture turned deep red. Silane (0.11 mmol) was added and the reaction mixture was heated for the indicated period of time. The conversion of the substrate was determined by ¹H NMR spectroscopy.

Crystal structure determination

X-ray diffraction data were collected on a Bruker D8 goniometer with APEX CCD area-detector in ω -scan mode. Mo-K_{α} radiation (multilayer optics, $\lambda = 0.71073$ Å) from an Incoatec microsource was used. Temperature control was achieved with an Oxford cryostream 700.

Determination of the unit cells of 2β , 3β and 4 and frame processing was done with SAINT+.39 The low temperature structures were indexed with CELL NOW.40 Multiscan absorption corrections were applied with SADABS⁴¹ for single crystal data and TWINABS⁴² for the twinned data. Structures were solved by direct methods (SHELXS⁴⁰) and refined against F^2 with SHELXL-13.40 Hydrogen atoms were included as riding on calculated positions with $U_{iso}(H) = 1.2U_{eq.}(non-H)$. Nonhydrogen atoms were refined with anisotropic displacement parameters in the well ordered parts. The disordered parts were modeled using one isotropic displacement parameter for all atoms in the disordered molecular fragment. In 2β all non-H atoms of the crown ether could be found in the difference Fourier map. In 3β only 1 reasonably high electron density maximum could be found and the crown ether was constructed based on this position. Restraints were slowly released to allow for stable refinement. In the final model of both structures C-C distances are restrained to be close to 1.42 Å and C-O distances to 1.50 Å. The disordered thf molecules are based on a constructed model that was placed in the void with diffuse electron density and refined with the same distance restraints. Full details of the refinement are given as ESI.†

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