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A supramolecular approach to zwitterionic alkaline metal silanides and formation of heterobimetallic silanides[†]

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Incorporating pendant polydonor groups is key to the synthesis and isolation of a series of novel and truly zwitterionic alkaline metal silanides of formula $Si[SiMe_2O(CH_2)_nOMe]_3$ (n = 2, 3; M = Li, Na, K) that can easily be converted into heterobimetallic silanides.

Zwitterionic metal silanides¹ represent a structurally novel class of tri-coordinated silvl anions² in which the cationic metal center is separated from the silicon anion by internal donor bridges. In striking contrast to the well-documented family of tetra-coordinate borate based zwitterions,³ silanides have a stereo-chemically active electron pair localized at the central silicon anion, which is available for additional metal binding. In fact, our recent studies on the structures of the metal silanides, $[Si(SiMe_2OMe)_3]M$ (M = Li, Na, K), have shown that the anionic silicon can compete with the internal methoxy donors for the coordination sphere of the metal cation resulting in highly aggregated structures.^{1b} Herein, we report on the synthesis and structure of a series of discrete zwitterionic alkali metal silanides with pendant polydonor groups that exclusively bind to the metal cation. This type of supramolecular approach not only avoids self-aggregation it also leaves the central anionic silicon "naked" which enables zwitterionic heterobimetallic silanides, a hitherto unknown class of silanide complexes, to be synthesized.

The synthetic route to the novel zwitterionic alkaline metal silanides M-4 and M-5 (M = Li, Na, K) is outlined in Scheme 1. Reaction of Si(SiMe₂Cl)₄ (1) with 2-methoxy-ethane-1-ol or 3-methoxy-propane-1-ol in the presence of triethylamine gave the neutral precursor compounds $Si(SiMe_2O(CH_2)_2OMe)_4$ (2) and $Si(SiMe_2O(CH_2)_3OMe)_4$ (3) as colourless liquids in good yields. Upon treatment of 2 and 3, respectively, with MOBu^t (M = Li, Na, K) in THF at room temperature, the zwitterionic lithium, sodium and potassium silanides {Si[SiMe_2O(CH_2)_2OMe]_3}M, (M-4), and {Si[SiMe_2O(CH_2)_3OMe]_3}M, (M-5), were generated.



Scheme 1 Synthesis of M-4 and M-5.

These Si–Si bond cleavage reactions⁴ proceeded selectively with elimination of Bu^tOSiMe₂OR [R = $(CH_2)_2OMe$, $(CH_2)_3OMe$] within *ca*. two hours and were essentially quantitative according to ¹H-NMR spectroscopic measurements. M-4 and M-5 are highly moisture and oxygen sensitive and spontaneously selfignite upon exposure to air.⁵ They are, however, thermally stable and can be re-crystallized from hot hexanes.

The solid-state structures of Li-4, Na-4, K-4 and Na-5 were determined by X-ray crystallography, and the results for Na-4 and Na-5 are shown in Fig. 1 and 2 along with selected average distances and angles of all four structures (Table 1). The X-ray



Fig. 1 Structure of Na-4 in the crystal (black = carbon, white = hydrogen).

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Fig. 2 Structure of Na-5 in the crystal (black = carbon, white = hydrogen).

Table 1Selected average distances [Å] and angles [°] of Li-4, Na-4,Na-5 and K-4

	Li-4	Na-4	Na-5	K-4
Si–Si	2.32	2.32	2.32	2.32
Si-O	1.69	1.68	1.68	1.68
M-O _(SiOC)	2.08	2.32	2.35	2.74
M-O _(COC)	2.24	2.38	2.40	2.74
M-Sil	3.92	4.00	3.98	4.50
Si-Si-Si	96	99	100	100
Si–Si–O	113	113	113	113
Si-O-M	126	122	124	125

data of all structurally characterized metal silanides confirm the expected tripodate structure. The three bidentate methoxyalkoxide groups of the podand are dicoordinated to the metal cation whose coordination sphere is best described as distorted octahedral. Regardless of the identity of the metal ion being incorporated, the average Si–Si [2.32 Å], Si–O [1.68–1.69 Å] distances and Si–Si–O [113°], Si–O–M [122–126°] angles are all very similar to each other; only the M–O distances expectedly increase as the size of M increases. Interestingly, the Si–Si-Si angles are significantly reduced from an ideal tetrahedral value of 109.5° to an average value of *ca*. 100° for Na-4, K-4 and Na-5, and 95.5° for Li-4, which we ascribe to both the presence of an electron pair at the central silicon Si1 and M–O interactions which decrease the angles as the size of the metal decrease.⁶

The M–Sil distances in the zwitterions Li-4 (3.92 Å), Na-4 (4.00 Å), K-4 (4.50 Å) and Na-5 (3.98 Å) are significantly longer than that in the previously reported non-zwitterionic silanides $[(Me_3Si)_3SiLi]_2$ (Li-6) (2.60 Å), $[(Me_3Si)_3SiNa]_2$ (Na-6) (3.00 Å) and $[(Me_3Si)_3SiK]_2$ (K-6) (3.42 Å),⁷ where the metal cation is in close proximity to the silicon anion. The M–Sil distances of M-4/5 *versus* $[(Me_3Si)_3SiM]_2$ (M-6) are increased by a factor of ~1.5 for Li, ~1.32 for Na and ~1.32 for K. These values provide a good estimate on the extent of charge separation in zwitterionic species relative to their non-zwitterionic counterparts M-6 and reveal that the

Table 2 29 Si-NMR shifts [ppm] of the central silicon anions of 4–6 measured in C₆D₆ at 300 K

	M = Li	M = Na	M = K		
	-215.3^{a} -215.4^{a} -181.9^{b}	-204.5^{a} -200.3^{a} -179.8^{c}	-194.1^{a} -194.7^{a} -185.7^{c}		
^a This work. ^b Taken from ref. 9. ^c Taken from ref. 7.					

separation of the formal charges is most pronounced in Li-4 and Li-5.

Notably, the order in M-Si1 distance, Li-Si1 > Na-Si1 > K-Si1, seems to be reflected also in the ²⁹Si-NMR chemical shifts of the central anionic silicon atoms of M-4 and M-5. For comparison, the values are shown in Table 2 along with those of the non-zwitterionic silanides 6. The data clearly show that the chemical shift of the anionic silicon decreases in the order K > Na > Li as the M–Si1 distance in M-4 and M-5 increases. This is consistent with theoretical studies on the ²⁹Si-NMR chemical shifts of hypersilanides that show the free silicon anion, $(Me_3Si)_3Si^-$, to have the lowest value with *ca*. -264 ppm.⁸ For non-zwitterionic silanides such as M-6, the chemical shift of the anionic silicon would be expected to be in the opposite order Li > Na > K, providing that in solution the cation is in close proximity to the anion as observed in solvent separated ion pairs (SSIP's) or contact ion pairs (CIP's). However, the signals of the central anionic silicon of M-6 do not show the expected chemical shift trend, instead the anionic silicon of Li-6 is slightly up-field shifted relative to that of Na-6, which perhaps is due to subtle structural changes of these species in solution.

To determine the stability of the new podands Si[SiMe₂O(CH₂)₂OMe]₃⁻ (4⁻) and Si[SiMe₂O(CH₂)₃OMe]₃⁻ (5^{-}) with respect to cation exchange, NMR-scale reactions of Li/Na-4 and Li/Na-5 with metal alkoxides and crown ethers were carried out and monitored by ⁷Li- and ²³Na-NMR (Scheme 2). For example, when Li-4 was mixed with one equivalent of either NaOBu^t or KOBu^t, rapid cation exchange was observed to quantitatively give the zwitterions Na-4 and K-4, respectively (eqn (1) and (2)). Clearly this exchange process is driven by the high binding affinity of a hard tert-butoxide anion to the hard lithium ion.¹⁰ On the other hand, no chemical shift change was observed in the ⁷Li-NMR spectra upon adding one equivalent of 15-crown-5 to C₆D₆ solutions of the zwitterionic silanides Li-4 and Li-5, suggesting no exchange reaction because of a strong ligand to metal binding (eqn (3) and (4)). In striking contrast, the ²³Na-NMR signal of Na-5 shifted instantly after adding one equivalent of 18-crown-6 from 2.5 ppm to -15.4 ppm. Based on comparison with previous data on the ²³Na-NMR chemical shifts of sodium crown ether complexes, the observed signal at

Li- 4 + NaOBu ^t	\longrightarrow	Na- 4 + LiOBu ^t	(Eq. 1)
Li- 4 + KOBu ^t		K- 4 + LiOBu ^t	(Eq. 2)
Li-4 + 15-crown-5	→	(15-crown-5)Li⁺ + 4 ⁻	(Eq. 3)
Li- 5 + 15-crown-5	→	(15-crown-5)Li ⁺ + 5 ⁻	(Eq. 4)
Na-4 + 18-crown-6		(18-crown-6)Na ⁺ + 4 ⁻	(Eq. 5)
Na-5 + 18-crown-6		(18-crown-6)Na ⁺ + 5 ⁻	(Eq. 6)

Scheme 2 Cation exchange chemistry of M-4 and M-5.



Fig. 3 Temperature dependent ²³Na-NMR spectra of a 1 : 1 mixture of 18-crown-6 and Na-4 in THF.

-15.4 ppm can be assigned to the sodium ion crown ether complex, (18-crown-6)Na⁺ (eqn (6)).^{11,12}

Zwitterion Na-4 (eqn (5)) behaves somewhat differently as the sodium signal in THF only slightly shifts to higher field from 0.4 ppm to -2.5 ppm, but broadens tremendously upon adding 18-crown-6 indicating slow exchange occurring at room temperature (Fig. 3). Moreover, upon cooling progressively to -20 °C the broad signal splits into two distinct signals, a sharp one at 3.1 ppm and a broader one at -13.5 ppm, which can be ascribed to Na-4 and (18-crown-6)Na⁺ being in equilibrium. These NMR experiments reveal podand 4⁻ to be more stable with respect to cation exchange than 5⁻. Comparison of the X-ray data of Na-4 with Na-5, which show the average M–O distances of Na-4 to be significantly shorter than those of Na-5, supports this view.

We next examined the ability of the "naked" anionic silicon to function as an additional donor for the electrophilic main group and transition metal species (Scheme 3). We chose Li-4 as the starting material and were pleased to see that $B(C_6F_5)_3$ and AlMe₃ readily reacted to afford the first stable zwitterionic silyl borates and aluminates 7 and 8 in good yields as crystalline materials.¹³ Reaction with $W(CO)_6$ gives with loss of one molecule of CO the corresponding zwitterionic tungstenate complexe 7 and 9 are worth mentioning as they are stable on air for weeks without any sign of decomposition. The composition of 7–9 was unambiguously confirmed by multinuclear NMR spectroscopy and the results of elemental analysis.

In summary, we have reported a facile method for the preparation of a series of discrete zwitterionic alkali metal



silanides with pendant polydonor groups, including the first stable sodium and potassium species. Charge separation in these novel zwitterions is most pronounced for the lithium silanides, which is reflected in the significant up-field shift of the central "naked" silicon anion of Li-4 and Li-5 in the ²⁹Si-NMR relative to the sodium and potassium derivatives. The naked silicon anion is available for additional metal coordination as exemplarily shown for reactions of Li-4 with main group and transition metal fragments, leading to hitherto unknown zwitterionic heterobimetallic silanides. Studies regarding the synthesis of novel mono- and bimetallic transition-metal silanides and their use as molecular catalysts are currently underway.

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