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Preparation and structural characterisation of methoxybis(trimethylsilyl)silyl potassium and its condensation product

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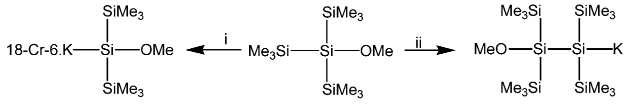
Depending on the conditions the reaction of tris(trimethylsilyl)methoxysilane (1) with potassium *tert*-butoxide either in benzene and in the presence of 18-crown-6 or in THF gives either the crown ether adduct of potassium-methoxybis(trimethylsilyl)silane (2), or 2-methoxytetrakis(trimethylsilyl)disilanyl potassium (3).

In recent years the chemistry of reactive functional intermediates has become an attractive area of organic synthesis. In organosilicon chemistry only a few α-functionalized silyl anions[1] have been prepared. Besides a considerable number of hydrogen bearing metalated silanes,[2,3] Tamao *et al.* were the first to systematically study α-heteroatom substituted silyl anions.[4,5] Initially investigated aminosilyllithium compounds were found to behave very much like ordinary silylanions with the gained advantage of simple replacement of the amino group by, for instance, halogen after the reaction of the silyl anion with an electrophile. Alkoxysilyl anions showed the additional feature of silylenoid (in analogy to carbenoid) behaviour, exhibiting both nucleophilic as well as electrophilic properties. This combination makes self-condensation a typical reaction for this type of compound. A recent example of an α-fluorosilyl anion from our laboratory showed the same type of chemistry in an even more pronounced fashion.[6] Previous work from our group has established the reaction of potassium *tert*-butoxide with oligosilanes as a convenient source of oligosilyl potassium compounds.[3,7] Employing this method we are able to provide the first structurally characterized example of an α-alkoxy silyl anion. By reaction of methoxytris(trimethylsilyl)silane (**1**) with potassium *tert*-butoxide in the presence of 18-crown-6 a clean reaction to the expected methoxybis(trimethylsilyl)silyl potassium (**2**) occurs (Scheme 1).† This is in accordance with the previously found diminished silylenoid character of crown ether adducts.[5a] The ^{29}Si NMR data of **2** display the already known phenomenon of a pronounced downfield shift of the metalated silicon atom (+32.3 ppm) compared to the precursor molecule **1** (+3.9 ppm). While this seems to be a typical feature of silylenoids it is in strong contrast to our previous observations on ordinary silyl anions which always show a strong upfield shift upon metalation.[3,7]

The crystal structure of **2**‡ (Fig. 1) shows coordination of both the anionic silicon and the alkoxy group to the potassium cation. The negatively charged silicon is quite pyramidal as the sum of the O–Si–Si and Si–Si–Si angles is 308.2°. A weak interaction between the potassium and a trimethylsilyl group of the neighbouring molecule can be observed.[7b]

2 can be reacted with various electrophiles such as trimethylsilylchloride, ethylbromide and sulfuric acid to give the respective derivatives: $(Me_3Si)_2(MeO)SiX$ (X = $SiMe_3$, Et, H).

A slight change in reaction conditions, employing THF as solvent without any crown ether causes the formation of a condensation product of **2**, namely 2-methoxytetrakis(trimethylsilyl)disilanylpotassium (**3**) (Scheme 1).† Mechanistically **3** is formed because of the ambiphilic character of the silylenoid **2**. In a nucleophilic displacement reaction one molecule of **2** serves as an electrophile which is attacked by another molecule of **2**. The involvement of a silylene, derived by elimination of potassium methoxide from **2** is rather unlikely as we do not observe a silylation insertion product with **1**.



2 1 3

Scheme 1 Formation of either α- or β-methoxyoligosilyl potassium compounds. i ^{t}BuOK, 18-crown-6, toluene r.t.; ii ^{t}BuOK, THF, r.t.

A single crystal structure analysis of **3**‡ reveals a dimerisation in the solid state with crystallographically imposed inversion symmetry between the two parts of the dimer. A considerable number of contacts can be observed (Fig. 2). The already known structural motif of a four-membered ring consisting of the Si–K–Si′–K′ sequence[8] is expanded by coordination of the alkoxy group and also the oxygen bearing silicon atom to the potassium atom. In addition some interaction with a trimethylsilyl group of a neighbouring cluster is detected.

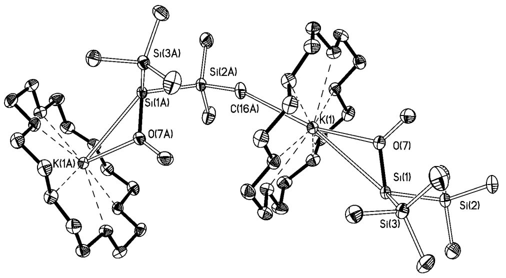


Fig. 1 Molecular structure of **2** with thermal ellipsoids at the 30% probability level (hydrogen atoms omitted for clarity). Selected bond distances (Å) and angles (°): K(1)–C(16A) 3.349(5), K(1)–O(7) 2.606(3), K(1)–Si(1) 3.5802(14), Si(1)–O(7) 1.754(3), Si(1)–Si(2) 2.3661(15), Si(1)–Si(3) 2.3682(16), O(7)–K(1)–Si(1) 27.63(6), C(16A)–K(1)–Si(1) 164.47(10), O(7)–Si(1)–Si(2) 103.46(11), O(7)–Si(1)–Si(3) 105.06(11), Si(2)–Si(1)–Si(3) 99.72(5), O(7)–Si(1)–K(1) 43.55(9), Si(2)–Si(1)–K(1) 129.06(5), Si(3)–Si(1)–K(1) 122.97(5), Si(1)–O(7)–K(1) 108.82(13). Symmetry transformations used to generate equivalent atoms: $(1/2-x, y-1/2, z)$.

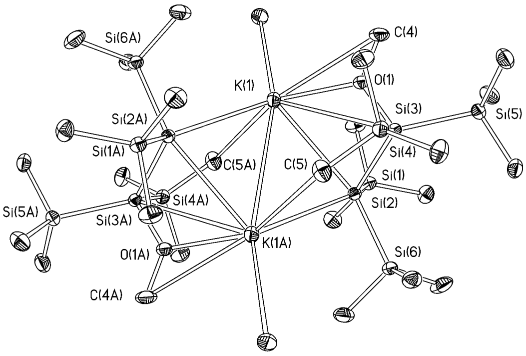


Fig. 2 Molecular structure of **3** with thermal ellipsoids at the 30% probability level (hydrogen atoms omitted for clarity). Selected bond distances (Å) and angles (°): K(1)–O(1) 2.584(2), K(1)–Si(2A) 3.4541(13), K(1)–Si(2) 3.5117(17), K(1)–Si(3) 3.6853(14), K(1)–K(1A) 4.1741(17), Si(1)–Si(2) 2.3361(13), Si(2)–Si(6) 2.3428(15), Si(2)–Si(3) 2.3507(13), Si(3)–Si(5) 2.3627(14), Si(3)–Si(4) 2.3699(13), Si(2A)–K(1)–Si(2) 106.38(3). Symmetry transformations used to generate equivalent atoms: $(1-x, -y, 1-z)$.

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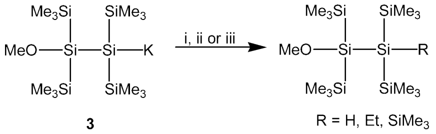

Scheme 2 Derivatisation reactions of **3**. i H_2SO_4; ii EtBr; iii Me_3SiCl.

A large ^{29}Si NMR downfield shift of the metalated silicon atom as observed for **2** (+32.3 ppm) cannot be found for **3**, which displays rather expected resonance values (*Si*O: +33.0, *Si*K: −170.4 ppm). Also **3** can be derivatised and reactions with trimethylsilylchloride, ethylbromide and sulfuric acid yield the expected products (Scheme 2).

The results described in this paper extend the chemistry of silylenoid compounds studied so far mainly by Tamao *et al.* into the area of oligosilanes.[4,5] It also provides the first structurally characterized examples of α-alkoxy silyl anions and the their condensation products. Our ongoing work will address the use of such compounds as transition metal ligands and as building blocks in oligo- and polysilane chemistry.

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Notes and references

† *Preparation of* **2**

To potassium *tert*-butoxide (39 mg, 0.35 mmol) and 18-crown-6 (92 mg, 0.35 mmol) in toluene (1.0 ml) was added methoxytris(trimethylsilyl)silane (100 mg, 0.36 mmol) in toluene (1.0 ml) dropwise at room temperature. The color of the solution immediatly became orange–red. After 1.5 h solvent and volatiles (^{t}BuOSiMe$_3$) were removed *in vacuo* to obtain **1** as an orange–red solid (165 mg, 92%). Single crystals for X-ray diffraction analysis were grown by dissolving the compound in a minimum amount of toluene. The dark red solution was stored at −70 °C for 15 days. Tiny cubic shaped crystals were obtained. ^{1}H NMR (300 MHz, C_6D_6) δ: 3.71 (s, 3 H, OCH_3), 3.23 (s, 24 H, OCH_2), 0.73 (s, 18 H, CH_3). ^{13}C NMR (75.4 MHz, C_6D_6) δ: 70.1, 62.6, 4.8. ^{29}Si NMR (59.3 MHz, C_6D_6) δ: 32.3 (*Si*–OCH$_3$), −14.7 (*Si*(CH$_3$)$_3$).

Preparation of **3**

To a solution of potassium *tert*-butanolate (39 mg, 0.36 mmol) in THF (1.0 ml) was added methoxytris(trimethylsilyl)silane (100 mg, 0.36 mmol) in THF (1.0 ml) dropwise at room temperature. The color of the solution immediately turned to orange. After 1.5 h solvent and volatiles (^{t}BuO-SiMe$_3$) were removed *in vacuo*. The residue was extracted with pentane and filtered. On evaporation of pentane **3** was obtained as an orange solid (70 mg, 93%). For X-ray diffraction analysis single crystals were grown by dissolution of **3** in a minimum amount of benzene. An equal amount of pentane was added to the solution and the vial was kept for two days under slow evaporation conditions in the glove box. ^{1}H NMR (300 MHz, C_6D_6) δ: 3.15 (s, 3 H, OCH_3), 0.50 (s, 18 H, CH_3), 0.44 (s,18 H, CH_3). ^{13}C NMR (75.4 MHz, C_6D_6) δ: 54.9 (O*C*H$_3$), 7.6 (*C*H$_3$)$_3$Si, 2.1 (*C*H$_3$)$_3$Si. ^{29}Si NMR (59.3, THF) δ: 33.0 (*Si*–OCH$_3$), −8.4 ((*Si*)$_2$–Si–OCH$_3$); −17.9 ((*Si*)$_2$–Si–K), −170.4 (K–*Si*–Si).

‡ Crystal data for $KSi_3O_7C_{19}H_{45}$ **2**: orthorhombic, space group *Pbca* (no. 61), a = 9.6523(19), b = 18.092(4), c = 34.297(7) Å, V = 5989(2) Å^3, Z = 8, d_c = 1.129 g cm^{-3}, μ = 0.328 mm^{-1}, (MoKα, λ = 0.71073 Å), T = 100 K, the structure was solved by direct methods and refined by full matrix least squares procedures: R_1 = 0.0741 and 0.0888 (wR_2 = 0.1520 and 0.1593) for 5291 unique measured reflections. CCDC number 232700.

Crystal data for $K_2Si_{12}O2C_{26}H_{78}$ **3**: monoclinic, space group $P2_1/n$ (no.14), a = 10.835(2), b = 17.659(4), c = 14.158(3) Å, β = 108.94(3)°, V = 2562.3(9) Å^3, Z = 2, d_c = 1.086 g cm^{-3}, μ = 0.486 mm^{-1}, (MoKα, λ = 0.71073 Å), T = 150 K, the structure was solved by direct methods and refined by full matrix least squares procedures: R_1 = 0.0539 and 0.0702 (wR_2 = 0.1076 and 0.1146) for 4368 unique measured reflections. CCDC number 232701. See http://www.rsc.org/suppdata/cc/b4/b406074a/ for crystallographic data in .cif or other electronic format.

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