Supporting Information

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General Remarks

The manipulation of air-sensitive compounds involved standard Schlenk line and Glove box techniques. THF, THF-D₈, benzene-D₆ and n-hexane were distilled under nitrogen from alkali metals and stored over molecular sieves prior to use. Si(SiMe₂Cl)₄ was synthesized as described in the literature [1]. The ¹H, ¹³C, ²⁹Si, ⁷Li and ²³Na NMR spectra were obtained from a Varian Unity Inova 500. All measurements, unless noted otherwise, were carried out at 300 K. The ⁷Li spectra were referenced to a 0.1 M solution of LiCl in D₂O (δ = 0), the ²³Na spectra to a 0.1 M solution of NaCl in D₂O (δ = 0) and the ¹¹B spectra to H₃BO₃ in D₂O (δ = 36 ppm), the ²⁷Al spectra to AlCl₃ in H₂O (δ = 0). Elemental Analyses were performed with a Perkin Elmer 2400 Series II CHNS/O Analyzer or by the Atlantic Microlab Inc.

Synthetic Procedures

Tetrakis(dimethyl-2-methoxyethoxysilyl)silane Si(SiMe₂OCH₂CH₂OCH₃)₄ (2)

NEt₃ (0.80 ml, 5.72 mmol) was added to a ice cooled hexanes solution of Si(SiMe₂Cl)₄ (510 mg, 1.27 mmol). To this solution HOCH₂CH₂OMe (2 ml, 25.4 mmol) was added dropwise and the resulting suspension was allowed to stir overnight at room temperature (the reaction was monitored by ¹H-NMR spectroscopy). After centrifugation, all volatiles were removed under vacuum. The liquid residue was distilled using a Kugelrohr (10⁻² mbar, 150-160°C) to afford 650 mg (91%) of the title compound as a colorless liquid. ¹H NMR (C₆D₆, 300 MHz): δ 0.58 (s, SiMe₂, 24 H), 3.15 (s, OCH₃, 12 H), 3.38 3.79 (2t, SiOCH₂CH₂O, 2 × 8 H) ppm. ¹³C NMR (C₆D₆, 125.7 MHz): δ 4.0 (SiMe₂), 58.6 (OMe), 62.9 (OCH₂), 74.3 (CH₂OMe) ppm. ²⁹Si NMR (C₆D₆, 99.3 MHz): δ 23.0 (SiMe₂O), -139.3 (SiSi₄) ppm. Anal. Calc. for C₂₀H₅₂O₈Si₅ (561.050): C, 42.82; H, 9.34. Found: C, 42.87; H, 9.13.
Tris(dimethyl-2-methoxyethoxysilyl)silyllithium Si(SiMe₂OCH₂CH₂OCH₃)₃Li (Li-4)

In a Glove box, a Schlenk flask with magnetic stirrer was filled with Bu⁴OLi (15 mg, 0.19 mmol) and Si(SiMe₂OCH₂CH₂OCH₃)₄ (100 mg, 0.18 mmol) and THF (1 ml) was added. After 1.5 hours, all volatiles were removed under vacuum (10⁻² mbar) to leave the title compound as a pale-yellow powder in almost quantitative yields. ¹H NMR (C₆D₆, 300 MHz): δ 0.63 (s, SiMe₂, 18 H), 2.93 (s, OCH₃, 9 H), 2.98 (t, CH₂O, 6 H), 3.38 (t, SiOCH₂, 6 H) ppm. ¹³C NMR (THF-D₈, 125.7 MHz): δ 5.1 (SiMe₂), 59.2 (OMe), 61.9 (OCH₂), 74.4 (CH₂OMe) ppm; ¹³C NMR (C₆D₆, 125.7 MHz): δ 5.2 (SiMe₂), 58.5 (OMe), 61.1 (OCH₂), 73.6 (CH₂OMe) ppm. ²⁹Si NMR (THF-D₈, 99.3 MHz): δ 48.1 (SiMe₂O), -213.1 (SiSi₃) ppm; ²⁹Si NMR (C₆D₆, 99.3 MHz): δ 45.8 (SiMe₂O), -215.3 (SiSi₃) ppm. ⁷Li NMR (THF-D₈, 194.2 MHz): δ -0.63 ppm; ⁷Li NMR (C₆D₆, 194.2 MHz): δ -1.02 ppm.

Tris(dimethyl-2-methoxyethoxysilyl)silylsodium Si(SiMe₂OCH₂CH₂OCH₃)₃Na (Na-4)

In a Glove box, a Schlenk flask with magnetic stirrer was filled with Bu⁴ONa (18 mg, 0.19 mmol) and Si(SiMe₂OCH₂CH₂OCH₃)₄ (100 mg, 0.18 mmol) and THF (1 ml) was added. After 1.5 hours, all volatiles were removed under vacuum (10⁻² mbar) to leave the title compound as a white powder in almost quantitative yields. ¹H NMR (C₆D₆, 300 MHz): δ 0.67 (s, SiMe₂, 18 H), 2.88 (s, OCH₃, 9 H), 2.93 (m, CH₂O, 6 H), 3.37 (m, SiOCH₂, 6 H) ppm. ¹³C NMR (C₆D₆, 125.7 MHz): δ 5.1 (SiMe₂), 58.2 (OMe), 60.9 (OCH₂), 74.4 (CH₂OMe) ppm. ²⁹Si NMR (C₆D₆, 99.3 MHz): δ 43.2 (SiMe₂O), -204.5 (SiSi₃) ppm. ²³Na NMR (C₆D₆, 132.2 MHz): δ -0.07 ppm.

Tris(dimethyl-2-methoxyethoxysilyl)silylpotassium Si(SiMe₂OCH₂CH₂OCH₃)₃K (K-4)

In a Glove box, a Schlenk flask with magnetic stirrer was filled with Bu⁴OK (21 mg, 0.19 mmol) and Si(SiMe₂OCH₂CH₂OCH₃)₄ (100 mg, 0.18 mmol) and THF (1 ml) was added. After 1.5 hours, all volatiles were removed under vacuum (10⁻² mbar) to leave the title compound as a white powder in almost quantitative yields. ¹H NMR (C₆D₆, 300 MHz): δ 0.71 (s, SiMe₂, 18 H), 2.84 (s, OCH₃, 9 H), 2.96 (m, CH₂O, 6 H), 3.42 (m, SiOCH₂, 6 H) ppm. ¹³C NMR (C₆D₆, 125.7 MHz):
MHz): $\delta$ 5.1 (SiMe$_2$), 57.8 (OMe), 61.1 (OCH$_2$), 74.9 (CH$_2$OMe) ppm. $^{29}$Si NMR (C$_6$D$_6$, 99.3 MHz): $\delta$ 39.5 (SiMe$_2$O), -194.1 (SiSi$_3$) ppm.

Tris(dimethyl-2-methoxyethoxysilyl)silane HSi(SiMe$_2$OCH$_2$CH$_2$OCH$_3$)$_3$ (H-4)

In a Glove box, a Schlenk flask with magnetic stirrer was filled with Bu'OLi (67 mg, 0.83 mmol) and Si(SiMe$_2$OCH$_2$CH$_2$OCH$_3$)$_4$ (457 mg, 0.82 mmol) and THF (5 ml) was added. After ca. 1.5 hours, NH$_4$Cl (54 mg, 1.01 mmol) was added at 0°C. The resulting suspension was allowed to stir at room temperature until the solution became colorless. All volatiles were removed under vacuum and hexane was added. After centrifugation, the solvent was removed under vacuum and the residue was distilled under vacuum using a Kugelrohrofen to afford 240 mg (69%) of the title compound as a colorless liquid. $^1$H NMR (C$_6$D$_6$, 300 MHz): $\delta$ 0.52 (s, SiMe$_2$, 18 H), 2.81 (s, SiH, 1 H), 3.13 (s, OCH$_3$, 9 H), 3.36 (t, CH$_2$O, 6 H), 3.77 (t, SiOCH$_2$, 6 H) ppm. $^{13}$C NMR (C$_6$D$_6$, 125.7 MHz): $\delta$ 3.5 (SiMe$_2$), 58.6 (OMe), 63.2 (OCH$_2$), 74.2 (CH$_2$OMe) ppm. $^{29}$Si NMR (C$_6$D$_6$, 99.3 MHz): $\delta$ 21.4 (SiMe$_2$O), -129.0 (d, $J_{Si-H} = 154.9$ Hz, SiH) ppm.

Tetrakis((3-methoxypropoxy)dimethylsilyl)silane Si(SiMe$_2$OCH$_2$CH$_2$CH$_2$OCH$_3$)$_4$ (3)

NEt$_3$ (9.8 ml, 70.4 mmol) was added to an ice-cooled hexanes solution of Si(SiMe$_2$Cl)$_4$ (2.83 g, 7.04 mmol). To this solution HOCH$_2$CH$_2$CH$_2$OMe (6.8 ml, 70.4mmol) was added dropwise and the resulting suspension was allowed to stir overnight at room temperature (the reaction was monitored by $^1$H-NMR spectroscopy). After centrifugation, all volatiles were removed under vacuum. The remaining residue was distilled using a Kugelrohrofen ($10^{-2}$ mbar, ca. 180°C) to afford 3.10 g (71%) of the title compound as a colorless liquid. $^1$H NMR (C$_6$D$_6$, 300 MHz): $\delta$ 0.55 (s, SiMe$_2$, 24 H), 1.84 (m, CH$_2$CH$_2$CH$_2$, 8 H), 3.15 (s, OCH$_3$, 12 H), 3.39, 3.76 (2t, CH$_2$O, SiOCH$_2$, 2 × 8 H) ppm. $^{13}$C NMR (C$_6$D$_6$, 125.7 MHz): $\delta$ 3.9 (SiMe$_2$), 33.4 (CH$_2$CH$_2$CH$_2$) 58.4 (OMe), 60.4 (OCH$_2$), 69.5 (CH$_2$OMe) ppm. $^{29}$Si NMR (C$_6$D$_6$, 99.3 MHz): $\delta$ 22.0 (SiMe$_2$O), -139.5 (SiSi$_4$) ppm. Anal. Calc. for C$_{24}$H$_{60}$O$_8$Si$_5$ (617.156): C, 46.71; H, 9.80. Found: C, 46.71; H, 9.63.
**Tris((3-methoxypropoxy)dimethylsilyl)silyllithium** \(\text{Si(SiMe}_2\text{OCH}_2\text{CH}_2\text{OCH}_3)_3\text{Li (Li-5)}\)

In a Glove box, a Schlenk flask with magnetic stirrer was filled with Bu'OLi (13 mg, 0.16 mmol) and Si(SiMe\(_2\)OCH\(_2\)CH\(_2\)CH\(_2\)OCH\(_3\))\(_4\) (100 mg, 0.16 mmol) and THF (1 ml) was added. After 1.5 hours, all volatiles were removed under vacuum (10\(^{-2}\) mbar) to leave the title compound as a pale-yellow powder in almost quantitative yields. \(^1\)H NMR (C\(_6\)D\(_6\), 300 MHz): \(\delta\) 0.65 (s, SiMe\(_2\), 18 H), 1.54 (m, CH\(_2\)CH\(_2\)CH\(_2\), 6 H), 3.04 (s, OCH\(_3\), 9 H), 3.05 (t, CH\(_2\)O, 6 H), 3.51 (t, SiOCH\(_2\), 6 H) ppm. \(^{13}\)C NMR (C\(_6\)D\(_6\), 125.7 MHz): \(\delta\) 5.2 (SiMe\(_2\)), 33.1 (CH\(_2\)CH\(_2\)CH\(_2\)), 58.8 (OMe), 62.1 (OCH\(_2\)), 71.2 (CH\(_2\)OMe) ppm. \(^{29}\)Si NMR (C\(_6\)D\(_6\), 99.3 MHz): \(\delta\) 45.3 (SiMe\(_2\)O), -215.4 (SiSi\(_3\)) ppm. \(^7\)Li NMR (C\(_6\)D\(_6\), 194.2 MHz): \(\delta\) -0.56 ppm.

**Tris((3-methoxypropoxy)dimethylsilylsodium** \(\text{Si(SiMe}_2\text{OCH}_2\text{CH}_2\text{OCH}_3)_3\text{Na (Na-5)}\)

In a Glove box, a Schlenk flask with magnetic stirrer was filled with Bu'ONA (16 mg, 0.17 mmol) and Si(SiMe\(_2\)OCH\(_2\)CH\(_2\)CH\(_2\)OCH\(_3\))\(_4\) (100 mg, 0.16 mmol) and THF (1 ml) was added. After 1.5 hours, all volatiles were removed under vacuum (10\(^{-2}\) mbar) to leave the title compound as a white powder in almost quantitative yields. \(^1\)H NMR (C\(_6\)D\(_6\), 300 MHz): \(\delta\) 0.69 (s, SiMe\(_2\), 18 H), 1.44 (m, CH\(_2\)CH\(_2\)CH\(_2\), 6 H), 2.97 (s, OCH\(_3\), 9 H), 3.13 (t, CH\(_2\)O, 6 H), 3.51 (t, SiOCH\(_2\), 6 H). \(^{13}\)C NMR (C\(_6\)D\(_6\), 125.7 MHz): \(\delta\) 5.0 (SiMe\(_2\)), 32.6 (CH\(_2\)CH\(_2\)CH\(_2\)), 58.2 (OMe), 61.9 (OCH\(_2\)), 72.4 (CH\(_2\)OMe) ppm. \(^{29}\)Si NMR (C\(_6\)D\(_6\), 99.3 MHz): \(\delta\) 42.0 (SiMe\(_2\)O), -200.3 (SiSi\(_3\)) ppm. \(^{23}\)Na NMR (C\(_6\)D\(_6\), 132.2 MHz): \(\delta\) 2.8 ppm.

**Tris((3-methoxypropoxy)dimethylsilylpotassium** \(\text{Si(SiMe}_2\text{OCH}_2\text{CH}_2\text{CH}_2\text{OCH}_3)_3\text{K (K-5)}\)

In a Glove box, a Schlenk flask with magnetic stirrer was filled with Bu'OK (19 mg, 0.17 mmol) and Si(SiMe\(_2\)OCH\(_2\)CH\(_2\)CH\(_2\)OCH\(_3\))\(_4\) (100 mg, 0.16 mmol) and THF (1 ml) was added. After 1.5 hours, all volatiles were removed under vacuum (10\(^{-2}\) mbar) to leave the title compound as a white powder in almost quantitative yields. \(^1\)H NMR (C\(_6\)D\(_6\), 300 MHz): \(\delta\) 0.69 (s, SiMe\(_2\), 18 H), 1.50 (m, CH\(_2\)CH\(_2\)CH\(_2\), 6 H), 2.99 (s, OCH\(_3\), 9 H), 3.23 (t, CH\(_2\)O, 6 H), 3.59 (t, SiOCH\(_2\), 6 H). \(^{13}\)C NMR (C\(_6\)D\(_6\), 125.7 MHz): \(\delta\) 6.0 (SiMe\(_2\)), 32.6 (CH\(_2\)CH\(_2\)CH\(_2\)), 58.2 (OMe), 60.6 (OCH\(_2\)), 71.0 (CH\(_2\)OMe) ppm. \(^{29}\)Si NMR (C\(_6\)D\(_6\), 99.3 MHz): \(\delta\) 37.1 (SiMe\(_2\)O), -194.7 (SiSi\(_3\)) ppm.
**Tris((3-methoxypropoxy)dimethylsilyl)silane HSi(SiMe₂OCH₂CH₂OCH₃)₃ (H-5)**

In a Glove box, a Schlenk flask with magnetic stirrer was filled with Bu<sup>1</sup>OLi (65 mg, 0.81 mmol) and Si(SiMe₂OCH₂CH₂OCH₃)₄ (500 mg, 0.81 mmol) and THF (5 ml) was added. After ca. 1.5 hours, NH₄Cl (54 mg, 1.01 mmol) was added at 0°C. The resulting suspension was allowed to stir at room temperature until the solution became colorless. All volatiles were removed under vacuum and hexane was added. After centrifugation, the solvent was removed under vacuum and the remaining residue was distilled under vacuum using a Kugelrohrofen to afford 350 mg (92%) of the title compound as a colorless liquid. <sup>1</sup>H NMR (C₆D₆, 300 MHz): δ 0.49 (s, SiMe₂, 18 H), 1.84 (m, CH₂CH₂CH₂, 6 H), 2.80 (s, SiH, 1 H), 3.12 (s, OCH₃, 9 H), 3.36 (t, CH₂O, 6 H), 3.76 (t, SiOCH₂, 6 H). <sup>13</sup>C NMR (C₆D₆, 125.7 MHz): δ 3.4 (SiMe₂), 33.3 (CH₂CH₂CH₂) 58.3 (OMe), 60.7 (OCH₂), 69.4 (CH₂OMe) ppm. <sup>29</sup>Si NMR (C₆D₆, 99.3 MHz): δ 20.2 (SiMe₂O), -130.3 (d, J<sub>Si-H</sub> = 154.9 Hz, SiH) ppm.

**(C₆F₅)₃BSi(SiMe₂OCH₂CH₂OMe)₃Li (7)**

B(C₆F₅)₃ (99 mg, 0.19 mmol) was added to Li-4 (83 mg, 0.19 mmol) dissolved in 1 mL of toluene and a precipitate formed immediately. The precipitate was centrifuged and washed several times with hexanes, and dried under vacuum to give a white powder of 7 in 89% yield. <sup>1</sup>H NMR (THF-D₈, 300 MHz): δ 0.08 (s, SiMe₂, 18 H), 3.41 (s, OCH₃, 9 H), 3.51 (t, SiOCH₂, 6 H), 3.70 (t, SiOCH₂, 6 H) ppm. <sup>13</sup>C NMR (THF-D₈, 125.7 MHz): δ 1.9 (SiMe₂), 59.5 (OMe), 61.4 (OCH₂), 73.3 (CH₂OMe), 136.5-149.8 (C₆F₅) ppm. <sup>29</sup>Si NMR (THF-D₈, 99.3 MHz): δ 34.2 (SiMe₂O), -129.0 (d, J<sub>Si-B</sub> = 146.8 Hz, SiSi₃) ppm. <sup>7</sup>Li NMR (THF-D₈, 194.2 MHz): δ -1.26 ppm. <sup>11</sup>B NMR (THF-D₈, 160.3 MHz): δ -4.9 ppm. <sup>19</sup>F NMR (THF-D₈, 282.3 MHz): δ -127.9 (br s, ortho-F), -164.3 (t, J<sub>F-F</sub> = 18.3 Hz, para-F), -167.5 (quint, J<sub>F-F</sub> = 18.3 Hz, J<sub>F-F</sub> = 26.0 Hz, meta-F) ppm - Anal. Calc. for C₃₃H₃₉BF₁₅LiO₆Si₄ (946.739): C, 41.87; H, 4.15. Found: C, 42.20; H, 4.25.
**Me₃AlSi(SiMe₂OCH₂CH₂OMe)₃Li (8)**

A toluene solution of AlMe₃ (0.08 mL, 2 M, 0.16 mmol) was added to Li-4 (70 mg, 0.16 mmol) dissolved in 1 mL of toluene and allowed to stay for 3 hours. After adding 2 mL of hexane colorless crystals were obtained, which were collected and dried under vacuum; yield 71%. Because the title compound slowly decomposes at room temperature over weeks, storage in a refrigerator at -30°C is recommended. ¹H NMR (C₆D₆, 300 MHz): δ 0.07 (s, AlMe₃, 9 H), 0.53 (s, SiMe₂, 18 H), 2.77 (m, OCH₃, CH₂O, 15 H), 3.15 (t, SiOCH₂, 6 H) ppm. ¹³C NMR (C₆D₆, 125.7 MHz): δ 3.8 (SiMe₂), 58.5 (OMe), 60.8 (OCH₂), 73.2 (CH₂OMe), -4.0 (AlMe₃) ppm. ²⁹Si NMR (C₆D₆, 99.3 MHz): δ 40.0 (SiMe₂O), -172.0 (SiSi₃) ppm. ⁷Li NMR (C₆D₆, 194.2 MHz): δ -1.66 ppm. ²⁷Al NMR (C₆D₆, 130.2 MHz): δ 155.0 ppm. All attempts to obtain satisfying elemental analysis data for 8 failed because of its thermal instability.

**W(CO)₆ (40 mg, 0.11 mmol) was added to a THF solution of Li-4 (50 mg, 0.11 mmol) at room temperature. After reacting overnight, the solvent was removed under vacuum and the residue was washed twice with hexanes to give the title compound as a pale yellow powder in almost quantitative yields. An analytically pure sample can be obtained by crystallization from toluene at room temperature. ¹H NMR: (THF-D₈, 300 MHz): δ 0.40 (s, SiMe₂, 18 H), 3.44 (s, OCH₃, 9 H), 3.51 (t, CH₂O, 6 H), 3.79 (t, SiOCH₂, 6 H) ppm. ¹³C NMR (THF-D₈, 125.7 MHz): δ 3.0 (SiMe₂), 59.5 (OMe), 62.3 (OCH₂), 74.1 (CH₂OMe), 203.3 (CO), 204.0 (CO) ppm. ²⁹Si NMR (THF-D₈, 99.3 MHz): δ 39.0 (SiMe₂O), -161.8 (SiSi₃) ppm. ⁷Li NMR (THF-D₈, 194.2 MHz): δ -1.0 ppm. Anal. Calc. for C₂₀H₃₉O₁₁Si₄Li₅W (758.640): C, 31.66; H, 5.18. Found: C, 31.62; H, 5.25.

NMR Tube Experiments

In a typical experiment, a THF solution of the zwitterionic sodium or lithium silanide was transferred to a J-Young NMR tube and the $^{23}\text{Na}$ or $^7\text{Li}$ NMR chemical shift was determined. Then equimolar amounts of crown ethers or metal alkoxides were added and again the $^{23}\text{Na}$ or $^7\text{Li}$ NMR chemical shifts were determined by NMR. The results are shown in Table 1.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Ratio</th>
<th>Chemical Shift</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Si(SiMe}_2\text{OCH}_2\text{CH}_2\text{OCH}_3)_3\text{Li (Li-4)}$</td>
<td>1 : 1</td>
<td>$\delta(\text{Li}) = -0.63$ ppm</td>
</tr>
<tr>
<td>$\text{Li-4} / 15\text{-crown-5}$</td>
<td>1 : 1</td>
<td>$\delta(\text{Li}) = -0.65$ ppm</td>
</tr>
<tr>
<td>$\text{Si(SiMe}_2\text{OCH}_2\text{CH}_2\text{OCH}_3)_3\text{Li (Li-5)}$</td>
<td>1 : 1</td>
<td>$\delta(\text{Li}) = -0.22$ ppm</td>
</tr>
<tr>
<td>$\text{Li-5} / 15\text{-crown-5}$</td>
<td>1 : 1</td>
<td>$\delta(\text{Li}) = -0.27$ ppm</td>
</tr>
<tr>
<td>$\text{Si(SiMe}_2\text{OCH}_2\text{CH}_2\text{OCH}_3)_3\text{Li (Li-4)}$</td>
<td>1 : 1</td>
<td>$\delta(\text{Li}) = -0.57$ ppm</td>
</tr>
<tr>
<td>$\text{Li-4} / \text{KOBu}^+$</td>
<td>1 : 1</td>
<td>$\delta(\text{Li}) = 0.62$ ppm</td>
</tr>
<tr>
<td>$\text{Si(SiMe}_2\text{OCH}_2\text{CH}_2\text{OCH}_3)_3\text{Li (Li-5)}$</td>
<td>1 : 1</td>
<td>$\delta(\text{Li}) = -0.56$ ppm</td>
</tr>
<tr>
<td>$\text{Li-5} / \text{NaOBU}^+$</td>
<td>1 : 1</td>
<td>$\delta(\text{Li}) = 0.53$ ppm, $\delta(\text{23Na}) = 0.44$ ppm</td>
</tr>
<tr>
<td>$\text{Si(SiMe}_2\text{OCH}_2\text{CH}_2\text{OCH}_3)_3\text{Na (Na-4)}$</td>
<td>1 : 1</td>
<td>$\delta(\text{23Na}) = 0.35$ ppm</td>
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<tr>
<td>$\text{Na-4} / 18\text{-crown-6}$</td>
<td>1 : 1</td>
<td>$\delta(\text{23Na}) = -2.46$ ppm</td>
</tr>
<tr>
<td>$\text{Si(SiMe}_2\text{OCH}_2\text{CH}_2\text{CH}_2\text{OCH}_3)_3\text{Na (Na-5)}$</td>
<td>1 : 1</td>
<td>$\delta(\text{23Na}) = 2.54$ ppm</td>
</tr>
<tr>
<td>$\text{Na-5} / 18\text{-crown-6}$</td>
<td>1 : 1</td>
<td>$\delta(\text{23Na}) = -15.36$ ppm</td>
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</tbody>
</table>
X-Ray studies

All crystallographic measurements were carried out on a Bruker APEX II diffractometer with a CCD area detector and Kα radiation at 150 K.

*Tris(dimethyl-2-methoxyethoxysilyl)silyllithium* Si(SiMe₂OCH₂CH₂OCH₃)₃Li (Li-4)

A plates-like specimen of C₁₅HLiO₆Si₄, approximate dimensions 0.18 mm x 0.21 mm x 0.37 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured.

The total exposure time was 4.07 hours. The frames were integrated with the Bruker SAINT software package using an Intensity data were corrected for Lorentz and polarization effects with SAINT V7.53A (Bruker AXS) using a narrow-frame integration algorithm. The integration of the data using a monoclinic unit cell yielded a total of 21754 reflections to a maximum θ angle of 23.73° (0.88 Å resolution), of which 3859 were independent (average redundancy 5.637, completeness = 100.0%, R_int = 3.85%, R_sig = 2.59%) and 3238 (83.91%) were greater than 2σ(F²). The final cell constants of a = 34.560(2) Å, b = 9.6993(7) Å, c = 17.1971(12) Å, β = 117.9710(10)°, volume = 5091.2(6) Å³, are based upon the refinement of the XYZ-centroids of 87 reflections above 20 σ(I) with 8.373° < 2θ < 36.88°. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.9115 and 0.9563.

The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group C 1 2/c 1, with Z = 8 for the formula unit, C₁₅HLiO₆Si₄. The final anisotropic full-matrix least-squares refinement on F² with 245 variables converged at R1 = 3.11%, for the observed data and wR2 = 7.75% for all data. The goodness-of-fit was 1.036. The largest peak in the final difference electron density synthesis was 0.291 e⁻/Å³ and the largest hole was -0.215 e⁻/Å³ with an RMS deviation of 0.040 e⁻/Å³. On the basis of the final model, the calculated density was 1.034 g/cm³ and F(000), 1584 e⁻.
**Fig. 1.** Molecular structure of Li-4 in the crystal; selected bond lengths [Å] and angles [°]: C7 O1 1.430(2), C7 C8 1.493(3), C8 O4 1.423(2), C9 O2 1.426(2), C9 C10 1.491(3), C10 O5 1.413(2), C13 O4 1.419(2), C14 O5 1.424(3), C15 O6 1.419(2), C16 O3 1.427(2), C16 C17 1.493(3), C17 O6 1.415(2), Li1 O2 2.076(3), Li1 O1 2.076(3), Li1 O3 2.091(3), Li1 O6 2.181(3), Li1 O4 2.235(3), Li1 O5 2.289(3), O1 Si2 1.6858(14), O2 Si3 1.6916(14), O3 Si4 1.6888(14), Si1 Si3 2.3175(8), Si1 Si4 2.3184(8), Si1 Si2 2.3186(8), O1 C7 C8 108.18(17), O4 C8 C7 107.29(16), O2 C9 C10 108.37(17), O5 C10 C9 108.03(17), O3 C16 C17 108.28(17), O6 C17 C16 108.05(16), O2 Li1 O1 97.09(14), O2 Li1 O3 95.52(14), O1 Li1 O3 93.49(14), O2 Li1 O6 156.32(18), O1 Li1 O6 105.87(14), O3 Li1 O6 77.63(12), O2 Li1 O4 104.19(14), O1 Li1 O4 76.17(12), O3 Li1 O4 158.64(17), O6 Li1 O4 87.16(12), O2 Li1 O5 76.19(11), O1 Li1 O5 160.82(18), O3 Li1 O5 104.94(14), O6 Li1 O5 83.65(12), O4 Li1 O5 87.95(12), C7 O1 Si2
122.93(12), C7 O1 Li1 107.80(14), Si2 O1 Li1 127.25(11), C9 O2 Si3 122.49(12), C9 O2 Li1 109.88(14), Si3 O2 Li1 125.28(12), C16 O3 Si4 122.45(12), C16 O3 Li1 109.08(14), Si4 O3 Li1 126.31(11), C13 O4 C8 111.67(16), C13 O4 Li1 131.97(16), C8 O4 Li1 111.55(14), C10 O5 C14 111.46(16), C10 O5 Li1 109.46(14), C14 O5 Li1 130.02(15), C17 O6 C15 112.45(16), C17 O6 Li1 111.44(14), C15 O6 Li1 131.21(15), Si3 Si1 Si4 96.33(3), Si3 Si1 Si2 95.18(3), Si4 Si1 Si2 95.27(3), O1 Si2 Si1 112.46(5), O2 Si3 Si1 112.75(5), O3 Si4 Si1 112.22(5).

Tris(dimethyl-2-methoxvethoxysilyl)silylsodium Si(SiMe\textsubscript{2}OCH\textsubscript{2}CH\textsubscript{2}OCH\textsubscript{3})\textsubscript{3}Na (Na-4):

A plates-like specimen of C\textsubscript{15}HNaO\textsubscript{6}Si\textsubscript{4}, approximate dimensions 0.10 mm x 0.17 mm x 0.48 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured.

The total exposure time was 4.07 hours. The frames were integrated with the Bruker SAINT software package using an Intensity data were corrected for Lorentz and polarization effects with SAINT V7.53A (Bruker AXS) using a narrow-frame integration algorithm. The integration of the data using a monoclinic unit cell yielded a total of 18024 reflections to a maximum θ angle of 24.97° (0.84 Å resolution), of which 3658 were independent (average redundancy 4.927, completeness = 78.2%, R\textsubscript{int} = 6.47%, R\textsubscript{sig} = 8.51%) and 2398 (65.55%) were greater than 2σ(F\textsuperscript{2}).

The final cell constants of a = 15.6614(18) Å, b = 9.8943(12) Å, c = 17.206(2) Å, volume = 2666.2(5) Å\textsuperscript{3}, are based upon the refinement of the XYZ-centroids of 53 reflections above 20 σ(I) with 8.064° < 2θ < 32.63°. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.8855 and 0.9756.

The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group P 1 21/c 1, with Z = 4 for the formula unit, C\textsubscript{15}HNaO\textsubscript{6}Si\textsubscript{4}. The final anisotropic full-matrix least-squares refinement on F\textsuperscript{2} with 245 variables converged at R1 = 3.51%, for the observed data and wR2 = 6.66% for all data. The goodness-of-fit was 0.815. The largest peak in the final difference electron density synthesis was 0.173 e\textsuperscript{-}/Å\textsuperscript{3} and the largest hole was -0.137 e\textsuperscript{-}/Å\textsuperscript{3} with an RMS deviation of 0.035 e\textsuperscript{-}/Å\textsuperscript{3}. On the basis of the final model, the calculated density was 1.028 g/cm\textsuperscript{3} and F(000), 824 e\textsuperscript{-}.
Fig. 2. Molecular structure of Na-4 in the crystal; selected bond lengths [Å] and angles [°]: Na1 O1 2.3166(17), Na1 O3 2.3205(17), Na1 O2 2.3292(19), Na1 O5 2.3698(19), Na1 O4 2.3785(17), Na1 O6 2.3891(18), Si1 Si3 2.3181(10), Si1 Si4 2.3183(10), Si1 Si2 2.3214(10), Si2 O1 1.6747(16), Si3 O2 1.6893(17), Si4 O3 1.6838(17), O1 C7 1.423(3), O2 C9 1.416(3), O3 C11 1.421(3), O4 C13 1.420(3), O4 C8 1.421(3), O5 C10 1.397(3), O5 C14 1.435(3), O6 C15 1.424(3), O6 C12 1.425(3), C7 C8 1.487(3), C9 C10 1.501(4), C11 C12 1.497(3), O1 Na1 O3 93.89(6), O1 Na1 O2 89.53(7), O3 Na1 O2 95.83(7), O1 Na1 O5 110.87(7), O3 Na1 O5 151.69(7), O2 Na1 O5 71.72(6), O1 Na1 O4 71.00(6), O3 Na1 O4 107.72(7), O2 Na1 O4 150.02(7), O5 Na1 O4 93.63(7), O1 Na1 O6 153.93(7), O3 Na1 O6 71.87(6), O2 Na1 O6 113.06(7), O5 Na1 O6 89.37(7), O4 Na1 O6 92.17(6), Si3 Si1 Si4 99.88(4), Si3 Si1 Si2
97.65(4), Si4 Si1 Si2 98.49(4), O1 Si2 Si1 112.92(6), O2 Si3 Si1 113.00(7), O3 Si4 Si1 113.32(6), C7 O1 Si2 124.92(13), C7 O1 Na1 106.29(13), Si2 O1 Na1 124.27(8), C9 O2 Si3 123.55(16), C9 O2 Na1 110.03(15), Si3 O2 Na1 121.02(9), C11 O3 Si4 124.77(14), C11 O3 Na1 107.46(13), Si4 O3 Na1 122.45(8), C13 O4 Na1 126.16(16), C8 O4 Na1 113.80(13), C10 O5 C14 113.5(2), C10 O5 Na1 112.27(14), C14 O5 Na1 122.86(19), C15 O6 C12 111.52(19), C15 O6 Na1 123.91(16), C12 O6 Na1 112.29(13).

Tris(dimethyl-2-methoxyethoxysilyl)silylpotassium \( \text{Si(SiMe}_2\text{OCH}_2\text{CH}_2\text{OCH}_3)_3K \) (K-4)

A cubic-like specimen of \( C_{15}H_{39}KO_6Si_4 \), approximate dimensions 0.22 mm x 0.28 mm x 0.33 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured.

The total exposure time was 4.07 hours. The frames were integrated with the Bruker SAINT software package using a Intensity data were corrected for Lorentz and polarization effects with SAINT V7.53A (Bruker AXS) using a narrow-frame integration algorithm. The integration of the data using a monoclinic unit cell yielded a total of 23434 reflections to a maximum \( \theta \) angle of 23.93° (0.88 Å resolution), of which 4105 were independent (average redundancy 5.709, completeness = 99.8%, \( R_{\text{int}} = 3.61\% \), \( R_{\text{sig}} = 2.48\% \)) and 3452 (84.09%) were greater than 2\( \sigma(F^2) \).

The final cell constants of \( a = 8.1549(6) \) Å, \( b = 19.2942(14) \) Å, \( c = 16.7811(12) \) Å, \( \beta = 90.9570(10)\° \), volume = 2640.0(3) Å\(^3\), are based upon the refinement of the XYZ-centroids of 104 reflections above 20 \( \sigma(I) \) with 4.489° < \( 2\theta < 39.31\° \).

The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group P 1 21/n 1, with \( Z = 4 \) for the formula unit, \( C_{15}H_{39}KO_6Si_4 \). The final anisotropic full-matrix least-squares refinement on \( F^2 \) with 245 variables converged at \( R1 = 2.86\% \), for the observed data and \( wR2 = 7.00\% \) for all data. The goodness-of-fit was 0.992. The largest peak in the final difference electron density synthesis was 0.257 e\(^-\)/Å\(^3\) and the largest hole was -0.158 e\(^-\)/Å\(^3\) with an RMS deviation of 0.040 e\(^-\)/Å\(^3\). On the basis of the final model, the calculated density was 1.175 g/cm\(^3\) and F(000), 1008 e\(^-\).
Fig. 3. Molecular structure of K-4 in the crystal; selected bond lengths [Å] and angles [°]: Si3 C3 1.880(2), Si3 C4 1.882(2), Si3 Si1 2.3185(8), Si2 O1 1.6800(14), Si2 Si1 2.3198(8), Si4 O3 1.6813(15), Si4 Si1 2.3191(8), O6 C12 1.407(3), O6 C15 1.415(3), O6 K1 2.7511(15), O5 C10 1.402(3), O5 C14 1.416(3), O5 K1 2.7238(15), O4 C13 1.408(3), O4 C8 1.413(3), O4 K1 2.7420(15), O2 C9 1.423(2), O2 K1 2.7607(14), O3 C11 1.420(2), O3 K1 2.7283(14), O1 C7 1.420(2), O1 K1 2.7611(14), O2 Si3 Si1 113.28(5), O1 Si2 C1 105.43(9), O1 Si2 C2 105.87(10), O1 Si2 Si1 113.10(5), O3 Si4 C6 105.55(9), O3 Si4 C5 105.94(10), O3 Si4 Si1 113.16(5), Si3 Si1 Si4 99.10(3), Si3 Si1 Si2 99.75(3), Si4 Si1 Si2 99.80(3), C12 O6 C15 112.92(19), C12 O6 K1 117.17(12), C15 O6 K1 126.99(16), C10 O5 C14 113.81(19), C10 O5 K1 118.67(12), C14 O5 K1 122.02(15), C13 O4 C8 113.29(17), C13 O4 K1 123.58(15), C8 O4 K1 118.31(12), C9 O2 Si3 124.03(13), C9 O2 K1 102.86(12), Si3 O2 K1 125.25(7), C11 O3 Si4
125.08(13), C11 O3 K1 102.57(12), Si4 O3 K1 126.04(7), C7 O1 Si2 124.19(13), C7 O1 K1 103.26(12), Si2 O1 K1 125.10(7), O2 C9 C10 109.22(19), O5 C10 C9 108.55(18), O3 C11 C12 109.65(18), O1 C7 C8 109.44(18), O6 C12 C11 108.80(18), O4 C8 C7 108.37(17), O5 K1 O3 140.27(5), O5 K1 O4 117.70(5), O3 K1 O4 95.46(5), O5 K1 O6 112.65(5), O3 K1 O6 60.39(4), O4 K1 O6 120.14(5), O5 K1 O2 60.52(4), O3 K1 O2 80.08(4), O4 K1 O2 140.72(4), O6 K1 O2 91.68(5), O5 K1 O1 96.88(5), O3 K1 O1 80.33(4), O4 K1 O1 60.33(4), O6 K1 O1 140.72(5), O2 K1 O1 80.54(4), O5 K1 Si1 80.78(3), O3 K1 Si1 130.44(3), O4 K1 Si1 77.42(3), O6 K1 Si1 80.87(4), O2 K1 Si1 134.17(3), O1 K1 Si1 130.94(3).

**Tris((3-methoxypropoxy)dimethylsilyl)silylsodium** Si(SiMe₂OCH₂CH₂OCH₃)₃Na (Na-5)

A prism-like specimen of C₁₈H₄₅NaO₆Si₄, approximate dimensions 0.20 mm x 0.27 mm x 0.30 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured.

The total exposure time was 4.07 hours. The frames were integrated with the Bruker SAINT software package using aIntensity data were corrected for Lorentz and polarization effects with SAINT V7.53A (Bruker AXS) using a narrow-frame integration algorithm. The integration of the data using a monoclinic unit cell yielded a total of 13489 reflections to a maximum θ angle of 22.15° (0.94 Å resolution), of which 2661 were independent (average redundancy 5.069, completeness = 74.0%, R_int = 5.95%, R_s = 7.85%) and 1839 (69.11%) were greater than 2σ(F²). The final cell constants of a = 11.248(4) Å, b = 15.467(5) Å, c = 16.551(5) Å, volume = 2879.4(15) Å³, are based upon the refinement of the XYZ-centroids of 8274 reflections above 20σ(I) with 4.922° < 2θ < 44.27°. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.9300 and 0.9516.

The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group P 1 21/n 1, with Z = 4 for the formula unit, C₁₈H₄₅NaO₆Si₄. The final anisotropic full-matrix least-squares refinement on F² with 271 variables converged at R1 = 3.29%, for the observed data and wR2 = 6.10% for all data. The goodness-of-fit was 0.830. The largest peak in the final difference electron density synthesis was 0.142 e/Å³ and the largest hole was -0.145 e⁻/Å³ with an RMS deviation of 0.030 e/Å³. On the basis of the final model, the calculated density was 1.137 g/cm³ and F(000), 1072 e⁻.
Fig. 2. Molecular structure of Na-5 in the crystal; selected bond lengths [Å] and angles [°]: C7 O1 1.422(3), C7 C8 1.531(4), C8 C9 1.516(4), C9 O4 1.431(4), C10 O2 1.427(3), C10 C11 1.520(4), C11 C12 1.525(4), C12 O5 1.417(3), C13 O3 1.437(3), C13 C14 1.514(4), C14 C15 1.525(4), C15 O6 1.423(3), C16 O4 1.420(4), C17 O5 1.406(3), C18 O6 1.424(3), Na1 O3 2.339(2), Na1 O1 2.339(2), Na1 O2 2.359(2), Na1 O5 2.387(2), Na1 O4 2.392(2), Na1 O6 2.414(2), O1 Si2 1.678(2), O2 Si3 1.684(2), O3 Si4 1.676(2), Si1 Si3 2.3134(13), Si1 Si2 2.3174(13), Si1 Si4 2.3237(14), O1 C7 C8 111.2(2), C9 C8 C7 111.8(3), O4 C9 C8 113.6(3), O2 C10 C11 111.1(2), C10 C11 C12 112.9(2), O5 C12 C11 113.4(3), C3 C13 C14 110.8(2), C13 C14 C15 112.8(2), O6 C15 C14 113.7(2), O3 Na1 O1 93.78(7), O3 Na1 O2 91.12(7), O1 Na1 O2 95.47(7), O3 Na1 O5 92.51(7), O1 Na1 O5 172.45(8), O2 Na1 O5 80.22(7), O3 Na1 O4
171.37(8), O1 Na1 O4 80.06(7), O2 Na1 O4 95.45(8), O5 Na1 O4 94.11(8), O3 Na1 O6 79.99(7), O1 Na1 O6 94.51(8), O2 Na1 O6 167.04(8), O5 Na1 O6 90.69(8), O4 Na1 O6 94.39(8), C7 O1 Si2 124.12(19), C7 O1 Na1 110.33(18), Si2 O1 Na1 125.09(10), C10 O2 Si3 124.16(17), C10 O2 Na1 110.38(16), Si3 O2 Na1 123.84(9), C13 O3 Si4 124.45(18), C13 O3 Na1 110.76(16), Si4 O3 Na1 123.57(10), C16 O4 C9 112.9(2), C16 O4 Na1 131.68(19), C9 O4 Na1 108.65(17), C17 O5 C12 113.9(2), C17 O5 Na1 132.15(19), C12 O5 Na1 108.82(17), C15 O6 C18 112.7(2), C15 O6 Na1 108.36(17), C18 O6 Na1 131.65(18), Si3 Si1 Si2 101.23(5), Si3 Si1 Si4 99.00(4), Si2 Si1 Si4 101.36(4), O1 Si2 Si1 113.07(7), O2 Si3 Si1 112.48(7), O3 Si4 Si1 113.98(8)