Supporting Information for the Manuscript

CS$_2$ activation at uranium(III) siloxide complexes: the effect of a Lewis acidic site

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A) NMR Spectra

Figure S1: $^1$H NMR spectrum (200 MHz, toluene-$d_8$, 298K) of the crude reaction mixture of CS$_2$ and 1 after 30 minutes.

Figure S2: $^1$H NMR spectrum (200 MHz, toluene-$d_8$, 298K) of the crude reaction mixture of CS$_2$ and 1 over the course of two days.
Figure S3: $^{13}$C($^1$H) NMR spectrum (400 MHz, pyridine-$d_5$, 298K) of the crystals of $[K(18-c-6)]C_2S_4.Py$ isolated from pyridine/hexane. (The same spectrum was measured for the solid obtained after washing with hexane of the crude obtained by evaporation of the toluene solution of 1 reacted with $^{13}$CS$_2$ for 30 minutes.)

Figure S4: Quantitative $^{13}$C NMR spectrum (400 MHz, DMSO-$d_6$, 298 K) of the reaction mixture between 1 eq. $^{13}$CS$_2$ and $[K(18c6)][U(OSi(O^tBU)_3)_4]$, 1 after 48 hours.
Figure S5: $^1$H NMR spectrum (200 MHz, toluene-$d_8$, 298 K) of the crude reaction mixture between 1 equiv. CS$_2$ and 2 over time.

Figure S6: $^{13}$C($^1$H) NMR spectrum (400 MHz, DMSO-$d_6$, 298K) of crystals of (C$_2$S$_4$)[K(DMSO)$_{1.5}$].
Figure S7: $^{13}$C NMR spectrum (400 MHz, DMSO-$d_6$, 298 K) of the crude reaction mixture between 4 equiv. of $^{13}$CS$_2$ and 2 after 48 hours.

**Table S1**: Ratio of the reaction products from the reactions of 1 and 2 with CS$_2$.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Eq. of CS$_2$</th>
<th>Ratio of CS$_3$</th>
<th>Ratio of C$_2$S$_4$</th>
<th>Ratio of C$_3$S$_5$</th>
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<tbody>
<tr>
<td>[U(OSi(OtBu)$_3$)$_4$][K18c6] 1</td>
<td>1</td>
<td>10</td>
<td>0</td>
<td>1</td>
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<tr>
<td>[U(OSi(OtBu)$_3$)$_4$][K18c6] 1</td>
<td>4</td>
<td>5</td>
<td>0</td>
<td>1</td>
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<tr>
<td>[U(OSi(OtBu)$_3$)$_4$K] 2</td>
<td>1</td>
<td>1</td>
<td>1.2</td>
<td>1</td>
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<tr>
<td>[U(OSi(OtBu)$_3$)$_4$K] 2</td>
<td>2</td>
<td>1</td>
<td>3.7</td>
<td>1</td>
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<tr>
<td>[U(OSi(OtBu)$_3$)$_4$K] 2</td>
<td>4</td>
<td>1</td>
<td>5.9</td>
<td>1</td>
</tr>
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</table>
B) Mass Spectrometry

Figure S8: ESI-MS spectrum of the reaction mixture between 1 and CS$_2$ in THF (positive ionization mode). Insert: zoom on the molecular peak compared with the theoretical isotopic profile calculated for [K(18-c-6)]$_2$[U(μ-η¹:η³CS$_3$)(OSi(OtBu)$_3$)$_4$-H]+ (3-H)$^+$. 

\[ [K(18-c-6)]_2[U(μ-η¹:η³CS$_3$)(OSi(OtBu)$_3$)$_4$-H]^+ \]
C) Crystallographic Data

Figure S9: Ellipsoid plot for of $[K_2C_2S_4(DMSO)]_n$, 5; probability 50%. Hydrogen atoms are omitted for clarity. (a) Asymmetric unit; (b) View of the 2-D coordination polymer.
Figure S10: Solid-state structure of \([\text{U(OSi(O^t\text{Bu})_3)}_4\text{K}_2(C_2S_3)]\), 6 showing the 1D-coordination polymeric arrangement. Hydrogen atoms are omitted for clarity.
Table S2. Crystallographic Data for Compounds 3-5.

<table>
<thead>
<tr>
<th></th>
<th>4. Py</th>
<th>3. 4 toluene</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula</td>
<td>C\textsubscript{31}H\textsubscript{53}K\textsubscript{2}NO\textsubscript{12}S\textsubscript{4}</td>
<td>C\textsubscript{101}H\textsubscript{188}K\textsubscript{2}O\textsubscript{28}S\textsubscript{3}Si\textsubscript{4}U</td>
<td>C\textsubscript{8}H\textsubscript{18}K\textsubscript{2}O\textsubscript{3}S\textsubscript{7}</td>
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<tr>
<td>Crystal size (mm)</td>
<td>1.07 x 0.13 x 0.02</td>
<td>0.544 x 0.440 x 0.349</td>
<td>0.522 x 0.265 x 0.020</td>
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<tr>
<td>cryst syst</td>
<td>Monoclinic</td>
<td>Triclinic</td>
<td>Triclinic</td>
</tr>
<tr>
<td>space group</td>
<td>C 2/c</td>
<td>P -1</td>
<td>P-1</td>
</tr>
<tr>
<td>volume (Å\textsuperscript{3})</td>
<td>4109.4(11)</td>
<td>6545.9(5)</td>
<td>1008.95(6)</td>
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<tr>
<td>a (Å)</td>
<td>23.321(3)</td>
<td>14.8483(6)</td>
<td>9.9182(3)</td>
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<td>b (Å)</td>
<td>10.1497(5)</td>
<td>17.9359(8)</td>
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<td>c (Å)</td>
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<tr>
<td>α (deg)</td>
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<td>81.725(4)</td>
<td>90.141(3)</td>
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<td>β (deg)</td>
<td>127.579(19)</td>
<td>85.150(3)</td>
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<td>γ (deg)</td>
<td>90</td>
<td>76.692(4)</td>
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<td>Z</td>
<td>4</td>
<td>2</td>
<td>2</td>
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<tr>
<td>formula weight (g/mol)</td>
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<td>2375.27</td>
<td>464.84</td>
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<tr>
<td>density (g cm\textsuperscript{-3})</td>
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<td>1.205</td>
<td>1.530</td>
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<td>absorption coefficient (mm\textsuperscript{-1})</td>
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<td>1.449</td>
<td>1.194</td>
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<td>F(000)</td>
<td>1776</td>
<td>2504</td>
<td>480</td>
</tr>
<tr>
<td>temp (K)</td>
<td>150.0(2)</td>
<td>150.0(2)</td>
<td>150.0(2)</td>
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<tr>
<td>total no. reflections</td>
<td>20966</td>
<td>59744</td>
<td>12179</td>
</tr>
<tr>
<td>unique reflections [R(int)]</td>
<td>5082 [R(int) = 0.0672]</td>
<td>26722 [R(int) = 0.0880]</td>
<td>6084 [R(int) = 0.0408]</td>
</tr>
<tr>
<td>Final R indices [I &gt; 2σ(I)]</td>
<td>R1 = 0.0611, wR2 = 0.1339</td>
<td>R1 = 0.0919, wR2 = 0.2028</td>
<td>R1 = 0.0472, wR2 = 0.0708</td>
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<tr>
<td>Largest diff. peak and hole e.Å</td>
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<td>3.509 and -1.881</td>
<td>0.459 and -0.400</td>
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<td>GOF</td>
<td>1.034</td>
<td>1.070</td>
<td>1.023</td>
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