## **Electronic Supplementary Information**

## Uranium(IV) Alkyl Complexes of a Rigid Dianionic NON-Donor Ligand: Synthesis and Quantitative Alkyl Exchange Reactions with Alkyl Lithium Reagents

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**Figures** 

- S1. Variable Temperature <sup>1</sup>H NMR spectra of  $[(XA_2)U(CH_2SiMe_3)_2]$  (1)
- S2. Variable Temperature <sup>1</sup>H NMR spectra of  $[Li(THF)_x][(XA_2)U(CH_2SiMe_3)_3]$  (3)
- S3. <sup>1</sup>H NMR spectrum of previously reported  $[(XA_2)Th(CH_2SiMe_3)_2]$  (1-Th)
- S4. <sup>1</sup>H NMR spectrum of in-situ generated [(XA<sub>2</sub>)Th(CH<sub>2</sub>SiMe<sub>3</sub>)(CH<sub>2</sub>CMe<sub>3</sub>)] (**5-Th**) as a 1:1 mixture with **2-Th** (as well as LiCH<sub>2</sub>SiMe<sub>3</sub> and LiCH<sub>2</sub>CMe<sub>3</sub>)
- S5. <sup>1</sup>H NMR spectrum of in-situ generated  $[(XA_2)Th(CH_2CMe_3)_2]$  (2-Th)
- S6. <sup>1</sup>H NMR spectrum of in-situ generated  $[Li(THF)_x][(XA_2)UMe_3]$  (4)

**Figure S1.** Variable Temperature <sup>1</sup>H NMR spectra of  $[(XA_2)U(CH_2SiMe_3)_2]$  (1) in toluene-*d*<sub>8</sub> (500 MHz). Signals for U-C*H*<sub>2</sub> protons, which are located at very high (>100 ppm) and very low (<-100 ppm) frequencies, are not shown.



**Figure S2.** Variable Temperature <sup>1</sup>H NMR spectra of  $[Li(THF)_x][(XA_2)U(CH_2SiMe_3)_3]$ (3; generated in situ from the reaction of 1 with LiCH\_2SiMe\_3) in THF-*d*<sub>8</sub> (500 MHz). Signals for U-C*H*<sub>2</sub> protons, which are located at very high (>100 ppm) and very low (<-100 ppm) frequencies, are not shown.





**Figure S3.** <sup>1</sup>H NMR spectrum of previously reported  $[(XA_2)Th(CH_2SiMe_3)_2]$  (**1-Th**) in toluene*d*<sub>8</sub> (600 MHz, 25°C). **Figure S4.** <sup>1</sup>H NMR spectrum (600 MHz, 25°C) of the reaction of  $[(XA_2)Th(CH_2SiMe_3)_2]$  (1-Th) with 2 equiv. LiCH<sub>2</sub>CMe<sub>3</sub> in toluene- $d_8$  to give a 1:1:3:1 mixture of  $[(XA_2)Th(CH_2CMe_3)_2]$ (2-Th),  $[(XA_2)Th(CH_2SiMe_3)(CH_2CMe_3)]$  (5-Th), eliminated LiCH<sub>2</sub>SiMe<sub>3</sub>, and remaining LiCH<sub>2</sub>CMe<sub>3</sub>. Peaks for 5-Th are identified in the spectrum below, and peaks are due to 2-Th are identified with an × symbol (see also Figure S5) (\* = toluene- $d_8$ ). Integration values are shown only for peaks due to 5-Th.



See page 6 for zoomed-in regions

## Figure S4 (continued)



**Figure S5.** <sup>1</sup>H NMR spectrum (600 MHz, 25°C) of the reaction of  $[(XA_2)Th(CH_2SiMe_3)_2]$ (1-Th) with 15 equiv. LiCH<sub>2</sub>CMe<sub>3</sub> in toluene-*d*<sub>8</sub> to give  $[(XA_2)Th(CH_2CMe_3)_2]$  (2-Th) and 2 equiv. of eliminated LiCH<sub>2</sub>SiMe<sub>3</sub> (in addition to 13 equiv. of remaining LiCH<sub>2</sub>CMe<sub>3</sub>). Integration values are shown only for peaks due to 2-Th. (\* = toluene-*d*<sub>8</sub>)



**Figure S6.** <sup>1</sup>H NMR spectrum of  $[Li(THF)_x][(XA_2)UMe_3]$  (**4**; generated in situ from the reaction of **1** with excess MeLi) in THF-*d*<sub>8</sub> (500 MHz, 25°C). Integration values are shown only for peaks due to **4**. Signals for U-C*H*<sub>3</sub> protons were not located between +400 and -400 ppm.

