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

Nicholas R. Andreychuk,[†] *Sougandi Ilango,*[†] *Balamurugan Vidjayacoumar,*[†] *David J. H. Emslie,**[†] *and Hilary A. Jenkins*[‡]

† Department of Chemistry and Chemical Biology, McMaster University, 1280 Main Street West, Hamilton, Ontario, L8S 4M1, Canada.

‡ McMaster University Analytical X-Ray Diffraction Facility, 1280 Main Street West, Hamilton, Ontario, L8S 4M1, Canada.

ABSTRACT

Reaction of $[(XA_2)UCl_3\{K(dme)_3\}]$ (XA_2 = 4,5-bis(2,6-diisopropylanilino)-2,7-di-*tert*-butyl-9,9-dimethylxanthene) with two equivalents of trimethylsilylmethyl lithium or neopentyl lithium afforded red-orange $[(XA_2)U(CH_2SiMe_3)_2]$ (**1**) and dark red $[(XA_2)U(CH_2CMe_3)_2]$ (**2**), respectively. Reaction of **1** with an additional equivalent of $LiCH_2SiMe_3$ in THF yielded yellow $[Li(THF)_x][(XA_2)U(CH_2SiMe_3)_3]$ (**3**), and reaction of $[(XA_2)UCl_3\{K(dme)_3\}]$ with three equivalents of methyl lithium in dme afforded yellow $[Li(dme)_3][(XA_2)UMe_3]$ (**4**). Reaction of **1** with 2.1 equivalents of $LiCH_2CMe_3$ in benzene resulted in rapid conversion to **2**, with release of two equivalents of $LiCH_2SiMe_3$. Similarly, reaction of **1** with 3.3 equivalents of MeLi in THF provided **4** as the $[Li(THF)_x]^+$ salt, accompanied by two equivalents of $LiCH_2SiMe_3$. These unusual alkyl exchange reactions resemble salt metathesis reactions, but with elimination of an alkyl lithium instead of a lithium halide. Addition of a large excess of $LiCH_2SiMe_3$ to **2** or **4** did not generate detectable amounts of **1** by NMR spectroscopy, suggesting that the equilibrium in these reactions lies far to the side of complexes **2** and **4**. By contrast, reaction of $[(XA_2)Th(CH_2SiMe_3)_2]$ (**1-Th**) with 2.2 equivalents of $LiCH_2CMe_3$ yielded an approximate 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**), $LiCH_2SiMe_3$ and $LiCH_2CMe_3$.

Introduction

The early actinide elements occupy a unique position in the periodic table where the *f*-orbitals have sufficient radial extension to interact with the ligands and can play an important role in bonding. Additionally, uranium is able to gain ready access to a significantly non-lanthanide-like range of oxidation states, from III to VI.[1] These attributes have the potential to lead to organometallic reactivity inaccessible with transition metal and lanthanide complexes, ideally resulting in new and productive applications for depleted uranium;[2] a byproduct of nuclear isotope enrichment that is currently stockpiled in large quantities. However, the organometallic chemistry of the actinide elements, relative to that of the transition metals and lanthanides, has been slow to develop, despite very early research efforts to prepare homoleptic actinide alkyl complexes[3-7] during the Manhattan project.[7,8] Consequently, the behaviour of actinide organometallic complexes in fields such as olefin polymerization, olefin hydroelementation, small molecule (e.g. carbon dioxide) activation, chemical vapor deposition (CVD) and atomic layer deposition (ALD) remains comparatively unexplored. Furthermore, the majority of actinide alkyl chemistry has involved carbocyclic ligand complexes, in particular cyclopentadienyl and cyclooctatetraenyl complexes.[8] In contrast, actinide alkyl complexes supported by multidentate non-carbocyclic ligand anions are scarce (Figure 1), despite the potential for such ligands to provide access to complexes with unique and readily tunable steric and electronic properties.

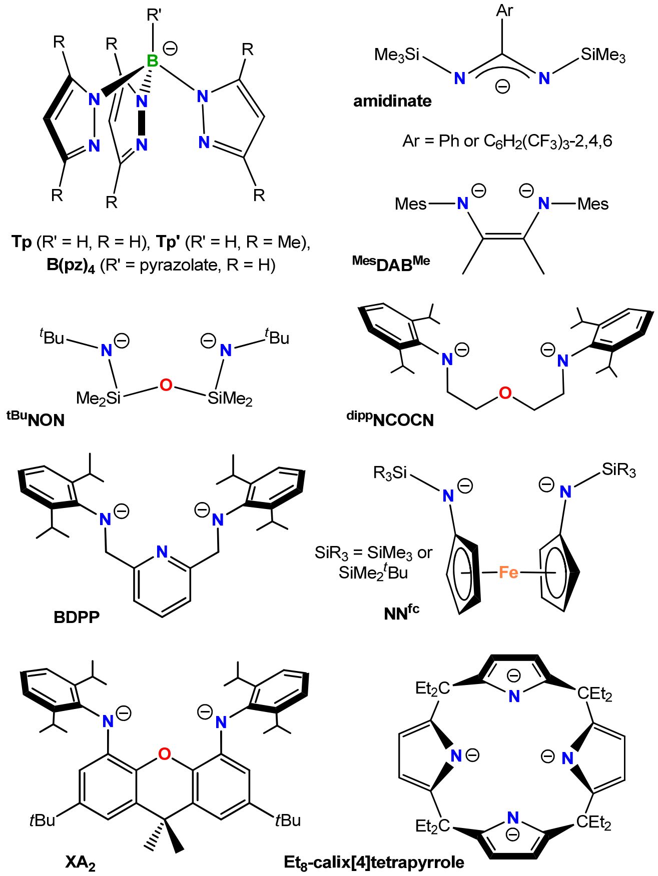


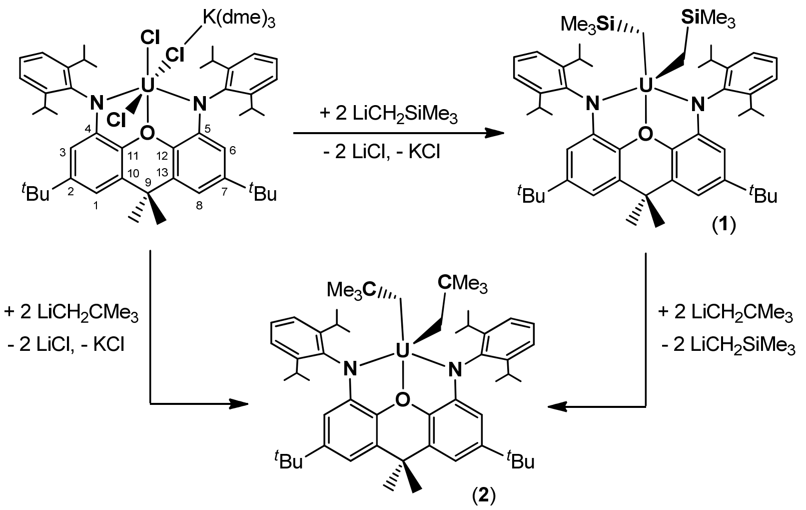
Figure 1. Multidentate anionic ligands previously employed in the synthesis of actinide alkyl[9] complexes: (a) Tp,[10] Tp',[11] and B(pz)$_4$ (pz = pyrazolate),[12] (b) amidinate,[13] (c) ^{Mes}DAB^{Me},[6] (d) ^{tBu}NON,[14,15] (e) ^{dipp}NCOCN,[15] (f) BDPP,[3,5,16,17] (g) NN^{fc},[5,18] (h) XA$_2$,[3,17,19] and (i) Et$_8$-calix[4]tetrapyrrole ligands.[20]

We have previously employed McConville's BDPP ligand and our own XA$_2$ ligand for the synthesis of neutral thorium(IV) bis-trimethylsilylmethyl and dibenzyl complexes, and these complexes were shown to exhibit high thermal stability, comparable to that of bis-pentamethylcyclopentadienyl analogues.[3,16,19] Reaction of the neutral thorium dialkyls with $B(C_6F_5)_3$ and $[CPh_3][B(C_6F_5)_4]$ provided access to the first non-cyclopentadienyl thorium alkyl cations, for example $[(XA_2)Th(CH_2SiMe_3)(\eta^6\text{-benzene})][B(C_6F_5)_4]$, and a rare example of a thorium dication, $[(XA_2)Th\{\eta^6\text{-}PhCH_2B(C_6F_5)_3\}_2]$.[17,19] We recently also prepared an NSN-donor analogue of the XA_2 ligand, TXA_2, and reported a study of U–O versus U–S covalency in tri- and tetravalent uranium XA_2 and TXA_2 chloro complexes.[21] Herein we describe the synthesis of neutral uranium(IV) dialkyl and anionic uranium(IV) trialkyl complexes prepared either from $[(XA_2)UCl_3\{K(dme)_3\}]$ by salt metathesis or from $[(XA_2)U(CH_2SiMe_3)_2]$ (**1**) via unusual alkyl exchange reactivity. For the purpose of comparison, the alkyl exchange reaction between $[(XA_2)Th(CH_2SiMe_3)_2]$ (**1-Th**) and $LiCH_2CMe_3$ was also investigated.

Results and Discussion

Reaction of $[(XA_2)UCl_3\{K(dme)_3\}]$ with 2 equivalents of $LiCH_2SiMe_3$ afforded highly soluble $[(XA_2)U(CH_2SiMe_3)_2]$ (**1**; Scheme 1), which was obtained as red-orange crystals in 64 % yield after crystallization from hexanes at –30 °C. The room temperature ^1H NMR spectrum of **1** in C_6D_6 or toluene-d_8 (Figure 2) shows only four signals: those for the *tert*-butyl groups, the *para*-positions of the 2,6-diisopropylphenyl rings, and the $CH^{1,8}$ and $CH^{3,6}$ positions of the xanthene backbone. These signals are unaffected by the top-bottom symmetry of the molecule, since they lie in the plane of the xanthene backbone of the ligand. All other signals are broadened into the baseline due to a fluxional process which exchanges the axial and in-plane CH_2SiMe_3 groups. However, at low temperature, a full complement of ^1H NMR signals was observed, ranging from +180 to –225 ppm at –60 °C (Figure 2), and indicative of C_s symmetry.

Scheme 1. Synthesis of complexes **1** and **2**.


K(dme)3
Cl
Cl
Cl
U
N
N
O
1
2
3
4
5
6
7
8
9
10
11
12
13
tBu
tBu
+ 2 LiCH2SiMe3
- 2 LiCl, - KCl
Me3Si
SiMe3
(1)
+ 2 LiCH2CMe3
- 2 LiCl, - KCl
Me3C
CMe3
(2)
+ 2 LiCH2CMe3
- 2 LiCH2SiMe3

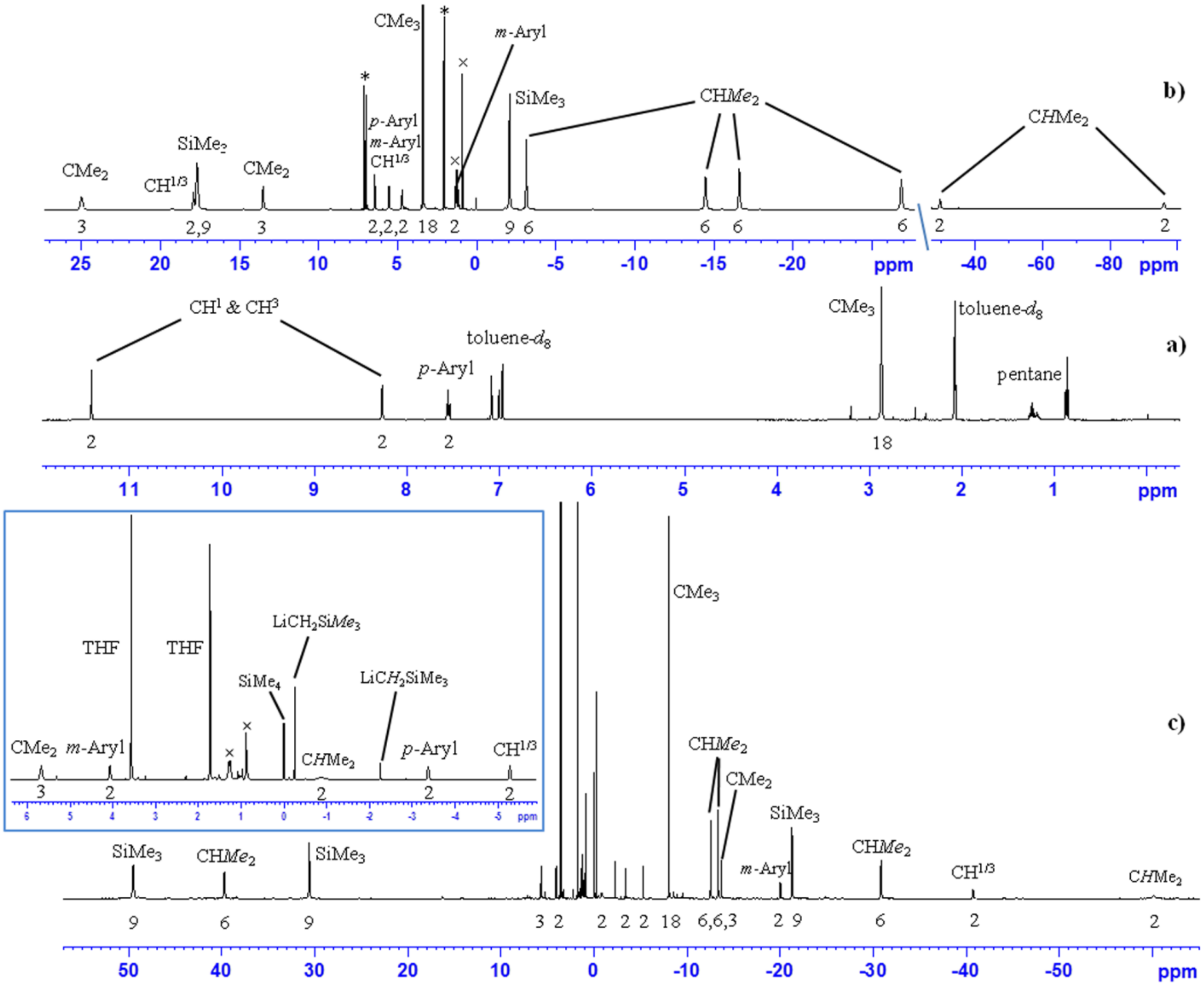

b)
CMe2
CH1/3
SiMe2
CMe2
p-Aryl
m-Aryl
CH1/3
CMe3
m-Aryl
SiMe3
CHMe2
CHMe2
3 2,9 3 2,2,2 18 2 9 6 6 6 6 2 2
25 20 15 10 5 0 -5 -10 -15 -20 ppm -40 -60 -80 ppm
a)
CH1 & CH3
p-Aryl
toluene-d8
CMe3
toluene-d8
pentane
2 2 2 18
11 10 9 8 7 6 5 4 3 2 1 ppm
c)
THF
THF
LiCH2SiMe3
SiMe4
LiCH2SiMe3
CMe2
m-Aryl
CHMe2
p-Aryl
CH1/3
3 2 2 2 2
6 5 4 3 2 1 0 -1 -2 -3 -4 -5 ppm
CMe3
CHMe2
CMe2
SiMe3
m-Aryl
SiMe3
CHMe2
SiMe3
CHMe2
CH1/3
CHMe2
9 6 9 3 2 2 2 2 18 6,6,3 2 9 6 2 2
50 40 30 20 10 0 -10 -20 -30 -40 -50 ppm

Figure 2. ^{1}H NMR spectra (500 MHz) of: (a) [(XA$_2$)U(CH$_2$SiMe$_3$)$_2$] (**1**) in toluene-*d*$_8$ at room temperature, (b) complex **1** in toluene-*d*$_8$ at –60 °C, and (c) *in-situ* generated [Li(THF)$_x$][(XA$_2$)U(CH$_2$SiMe$_3$)$_3$] (**3**) in THF-*d*$_8$ at –50 °C (in figure, * = toluene-*d*$_8$ and × = *n*-pentane). Numbers below the baseline indicate the integration of each peak. Signals for U-C*H*$_2$ protons, which are located at very high (>100 ppm) and very low (<–100 ppm) frequencies in spectra b and c, are not shown. The C*Me*$_3$ peaks are truncated in all three spectra, and the inset shows a portion of spectrum c.

The X-ray crystal structure of **1**·2(*n*-hexane) (Figure 3, Table 1) has two independent but structurally analogous 5-coordinate molecules in the unit cell, each with one CH$_2$SiMe$_3$ group in an axial position and one located approximately in the plane of the ancillary ligand backbone. The four anionic donors (we are not suggesting that **1** is 4-coordinate) adopt a distorted tetrahedral arrangement with N–U–N, C–U–C and N–U–C angles of 123.7(2)-123.9(2), 102.7(3)-105.4(3) and 101.1(2)-112.0(3)°, respectively. The neutral oxygen donor is located 0.92 and 0.95 Å out of the NUN-plane in the direction of the axial alkyl group, and the complex has approximate C_s symmetry, consistent with the low temperature NMR spectra.

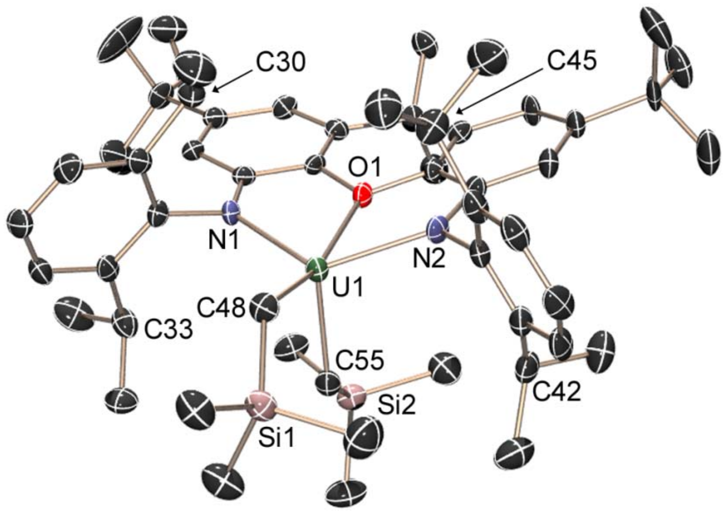


Figure 3. X-Ray crystal structure of $[(XA_2)U(CH_2SiMe_3)_2]\cdot 2(n\text{-hexane})$ $\{\mathbf{1}\cdot 2(n\text{-hexane})\}$ with thermal ellipsoids at 30% (collected at 173 K). Only one of the two independent molecules in the unit cell is shown. Hydrogen atoms and hexane solvent are omitted for clarity.

Complex number	**1-Th**	**1**	**2**	**4**	---
Complex	$(XA_2)Th(CH_2SiMe_3)_2$	$(XA_2)U(CH_2SiMe_3)_2$	$(XA_2)U(CH_2CMe_3)_2$	$(XA_2)UMe_3$ anion	$(XA_2)UCl_3K(dme)_3$
Lattice Solvent	toluene	2 *n*-hexane	*n*-hexane	dme	none
Reference	3[3]	this work	this work	this work	20[21]
An–O	2.535(4)	2.484(5), 2.504(4)	2.528(5), 2.529(5)	2.517(5)	2.465(3)
An–N	2.291(4), 2.312(4)	2.261(5), 2.262(5), 2.272(5), 2.280(5)	2.260(6), 2.272(6), 2.279(5), 2.289(6)	2.363(6), 2.373(6)	2.297(4), 2.306(4)
An–C_{axial} or An–Cl_{axial}	2.467(6)	2.368(7), 2.380(7)	2.386(8), 2.396(7)	U–C48 = 2.377(9) U–C50 = 2.493(8)	U–Cl2 = 2.620(2), 2.625(2) U–Cl3 = 2.629(2), 2.628(2)
An–$C_{in\ plane}$ or An–$Cl_{in\ plane}$	2.484(6)	2.393(7), 2.418(7)	2.409(7), 2.417(7)	U–C49 = 2.506(9)	U-Cl1 = 2.632(2), 2.619(3)
An–C–C_{axial} or An–C–Si_{axial}	126.8(3)	128.2(3), 130.4(3)	134.3(5), 134.4(5)	n/a	n/a
An–C–$C_{in\ plane}$ or An–C–$Si_{in\ plane}$	127.6(3)	130.5(4), 130.8(3)	130.3(5), 130.3(5)	n/a	n/a
C–An–C or Cl-An-Cl	111.9(2)	103.2(2), 105.0(2)	105.1(2), 106.6(3)	C48–U–C49 = 84.2(3) C49–U–C50 = 85.7(3) C48–U–C50 = 169.9(3)	Cl1–U–Cl2 = 89.91(6) Cl1–U–Cl3 = 88.25(6) Cl2–U–Cl3 = 177.07(6)
N–An–N	123.8 (2)	123.7(2), 124.0(2)	120.8(2), 120.9(2)	124.8(2)	129.1(1)
N–An–O	62.9(1), 63.0(1)	63.9(2), 64.0(2), 64.2(2), 64.4(2)	64.4(2), 64.5(2), 64.7(2), 65.1(2)	63.7(2), 63.8(2)	64.9(1), 65.5(1)
N–An–C_{axial} or N–An–Cl_{axial}	100.6(3), 100.8(2)	101.0(2), 101.6(2), 103.2(2), 103.3(2),	103.6(2), 105.5(2), 105.8(2), 108.5(2)	N–U–C48 = 92.4(2), 93.1(2) N–U–C50 = 90.5(2), 93.3(2)	N–U–Cl2 = 89.2(1), 92.5(1) N–U–Cl3 = 89.6(1), 90.3(1)
N–An–$C_{in\ plane}$ or N–An–$Cl_{in\ plane}$	109.1(2), 109.7(2)	108.1(2), 110.8(2), 111.7(2), 112.5(2)	107.6(2), 108.3(2), 109.2(2), 109.8(2)	N–U–C49 = 114.8(3), 120.3(3)	N–U–Cl1 = 114.6(1), 116.2(1)

O–(N/An/N-plane)	0.66	0.92	1.23, 1.29	0.75	0.53
An–(N/O/N-plane)	0.48	0.64, 0.65	0.84, 0.87	0.54	0.34
angle between xanthene aromatic rings	9.0	17.6, 19.0	33.4, 34.2	6.5	1.2
C(30)···C(45) or analogous in **1-Th**	4.00	4.63, 4.86	4.16, 4.22	7.30	6.87
C(33)···C(42) or analogous in **1-Th**	7.51	7.63, 7.70	8.01, 8.07	6.11	6.35
N(1)···N(2)	4.06	4.00, 4.02	3.95, 3.96	4.20	4.16

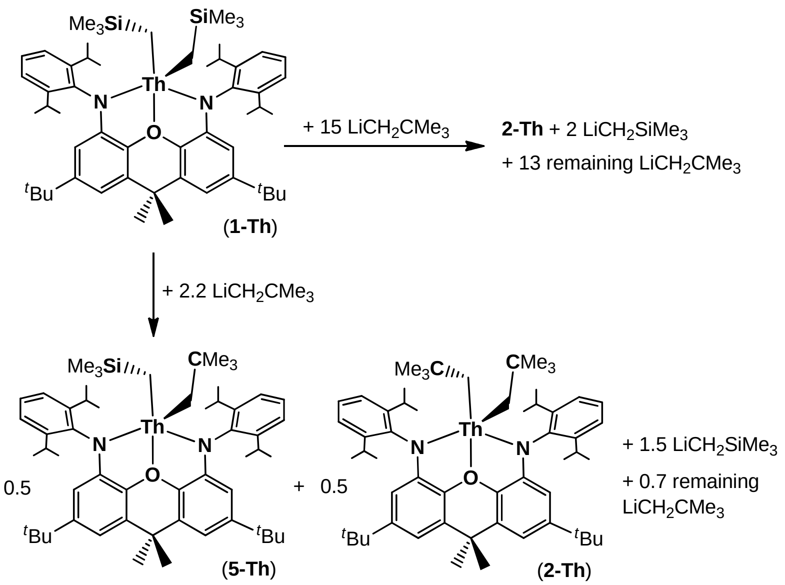
Table 1. Selected bond lengths (Å) and angles (°) for XA_2 complexes **1**, **2** and **4** as well as previously reported **1-Th** and $[(XA_2)UCl_3\{K(dme)_3\}]$.

The U–C distances of 2.368(7)-2.418(7) Å are comparable with those observed for the other crystallographically characterized neutral trimethylsilylmethyl uranium(IV) complex, Leznoff's $[\{(O(CH_2CH_2NAr)_2\}U(CH_2SiMe_3)_2]$ [Ar = 2,6-diisopropylphenyl; U–C = 2.40(2) and 2.44(2) Å], but are shorter than those in Hayton's anionic $[Li_{14}(O^tBu)_{12}Cl][U(CH_2SiMe_3)_5]$ [U–C = 2.445(6)–2.485(6) Å]. The U–C–Si angles of 128.2(3)-130.8(3)° are in line with previously reported values [125.7(3)-130.6(3)°], and the U–N distances are unremarkable.[21] However, as previously discussed in the context of $[(XA_2)UCl_3\{K(dme)_3\}]$, $[(XA_2)UCl(dme)]$,[21] and $[(XA_2)Th(CH_2SiMe_3)_2]$ (**1-Th**),[3] the An–O_{xant} distances in XA_2 actinide complexes [2.484(5) and 2.504(4) Å in **1**] are invariably shorter than might be expected for actinide–diarylether linkages, presumably due to steric constraints imposed by the rigid ligand framework.

The geometry of **1** is analogous to that of the thorium analogue, **1-Th**,[3,22] although the An–C, An–N and An–O distances in **1** are slightly shorter (Table 1), consistent with the smaller size of uranium [the 6-coordinate ionic radii for U^{4+} and Th^{4+} are 0.89 and 0.94 Å, respectively].[23] In addition, the xanthene backbone in **1** deviates further from planarity [the angle between the two aryl rings of the xanthene backbone is 17.6 and 19.0° for **1** versus 9.0° for **1-Th**], and uranium is positioned further from the NON-donor plane [0.64 and 0.65 Å for **1** versus 0.48 Å for **1-Th**]. However, the N1···N2 distance in **1** is only slightly shorter than that in the thorium analogue [4.00 and 4.02 Å in **1** versus 4.06 Å in **1-Th**], and the extent to which the 2,6-diisopropylphenyl groups are rotated away from the axial alkyl group is similar in **1** and **1-Th** [C(33)···C(42) = 7.63 and 7.70 Å and C(30)···C(45) = 4.63 and 4.86 Å in **1**; the corresponding distances in **1-Th** are 7.51 and 5.00 Å].

Addition of 2.1 equivalents of $LiCH_2CMe_3$ to $[(XA_2)U(CH_2SiMe_3)_2]$ (**1**) in C_6D_6 resulted in quantitative conversion to $[(XA_2)U(CH_2CMe_3)_2]$ (**2**) with release of two equivalents of $LiCH_2SiMe_3$ (Scheme 1). Treatment of complex **2** with up to 80 equivalents of $LiCH_2SiMe_3$ in C_6D_6 did not re-form detectable amounts of **1** by ^1H NMR spectroscopy, so the equilibrium in this reaction must lie far to the side of complex **2**. This unusual reaction bears resemblance to salt metathesis, but with elimination of $LiCH_2SiMe_3$ instead of a lithium halide. It is not unique to uranium, since the reaction between **1-Th** and 15 equivalents of $LiCH_2CMe_3$ cleanly provided $[(XA_2)Th(CH_2CMe_3)_2]$ (**2-Th**; Figure S5). However, addition of 2.2 equivalents of $LiCH_2CMe_3$ yielded an approximate 1:1:3:1 mixture of **2-Th**, $[(XA_2)Th(CH_2SiMe_3)(CH_2CMe_3)]$ (**5-Th**), $LiCH_2SiMe_3$ and $LiCH_2CMe_3$ (Scheme 2, Figure S4). This product distribution was established within 5 minutes and did not change with extended reaction times (days), consistent with a significantly smaller equilibrium constant for the reaction of **1-Th** with $LiCH_2CMe_3$, relative to the reaction of uranium complex **1** with $LiCH_2CMe_3$. Complex **5-Th** is the mixed alkyl species that must form *en route* from **1-Th** to **2-Th**, and both **2-Th** and **5-Th** were characterized in-situ by ^1H, ^{13}C and 2D NMR spectroscopy (at low temperature for **2-Th**).

Scheme 2. Reactions of **1-Th** with 2.2 and 15 equivalents of $LiCH_2CMe_3$



Complex **2** could also be prepared by a traditional salt metathesis reaction between [(XA$_2$)UCl$_3${K(dme)$_3$}] and two equivalents of LiCH$_2$CMe$_3$ (Scheme 1), and dark red crystals of **2**·*n*-hexane were obtained from a concentrated hexanes solution at –30 °C. Many of the peaks in the room temperature ^{1}H NMR spectrum of **2** are extremely broad, indicative of a fluxional process which exchanges the axial and in-plane alkyl groups, but as for complex **1**, a sharp spectrum consistent with C_s symmetry was observed at low temperature (Figure 4).

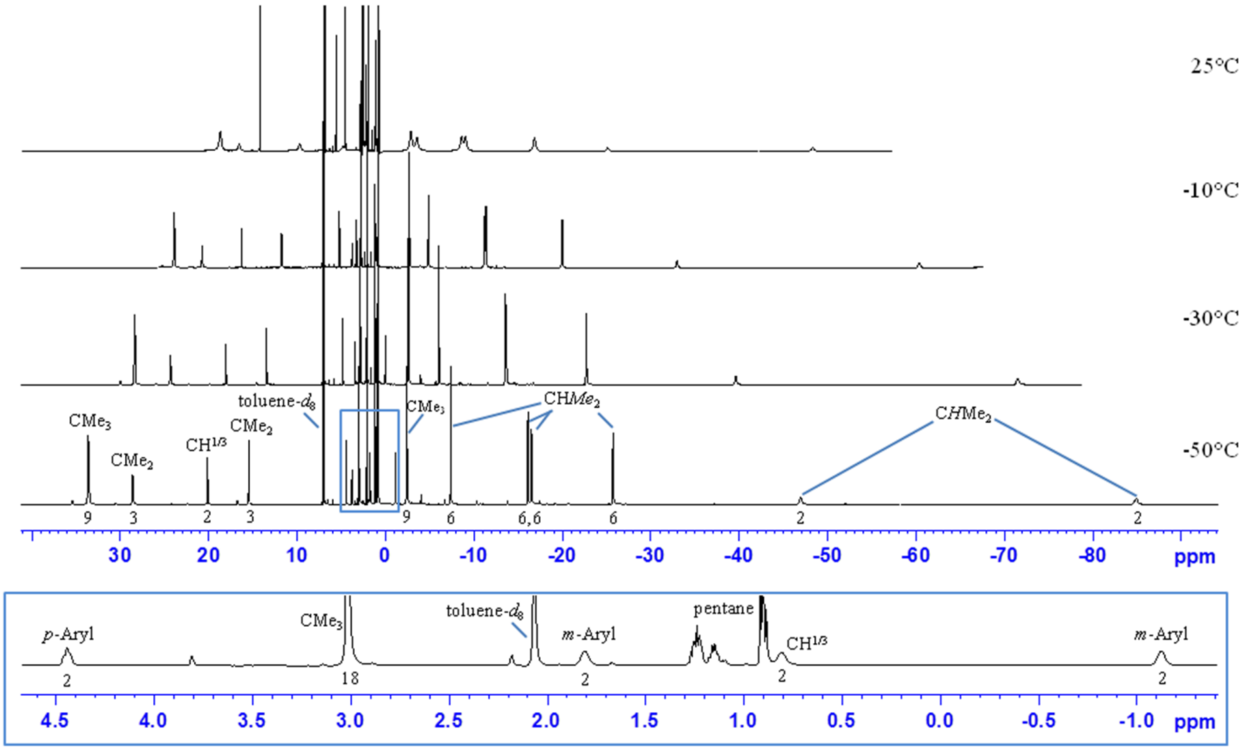


Figure 4. 500 MHz ^{1}H NMR spectra of [(XA$_2$)U(CH$_2$CMe$_3$)$_2$] (**2**) in toluene-d_8 at temperatures from 25 to –50 °C. Numbers below the baseline indicate the integration of each peak. Signals for U-CH_2 protons, which are located at very high (>100 ppm) and very low (<–100 ppm) frequencies, are not shown. The inset at the bottom shows a portion of –50 °C spectrum.

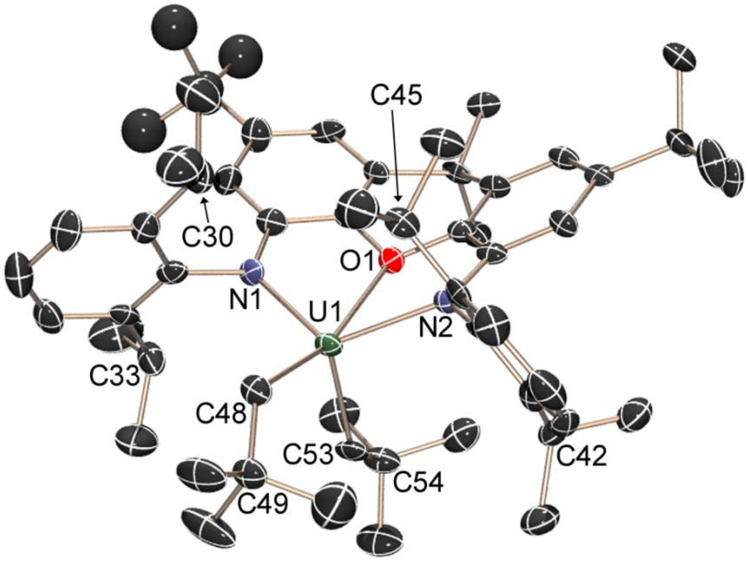


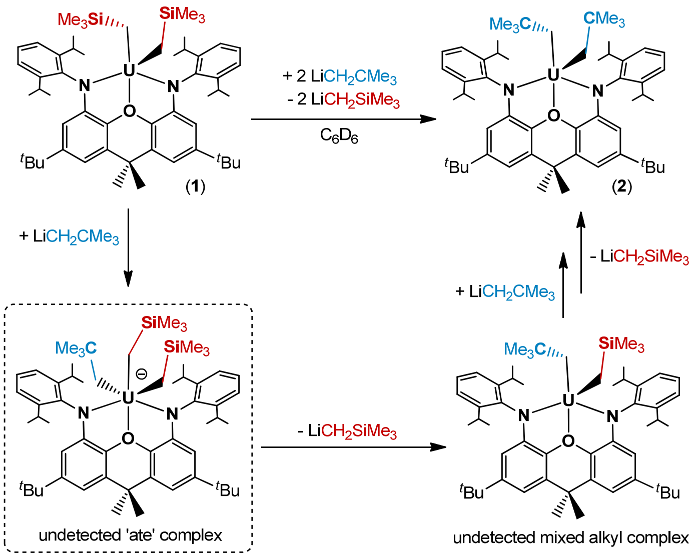
Figure 5. X-Ray crystal structure of $[(XA_2)U(CH_2CMe_3)_2]\cdot n$-hexane (**2**·*n*-hexane) with thermal ellipsoids at 50% (collected at 100 K). Only one of the two independent molecules in the unit cell is shown. Hydrogen atoms and hexane solvent are omitted for clarity. One *tert*-butyl group is disordered so was refined isotropically, and only one of the two orientations of the disordered *tert*-butyl group is shown.

The solid state geometry of complex **2** (Figure 5; Table 1) is analogous to that of **1**, and as with **1**, there are two independent but structurally analogous molecules in the unit cell. The U–C and U–N distances are comparable with those in **1**, despite the increased basicity of CH_2CMe_3 groups relative to CH_2SiMe_3 groups,[24] and the U–O distances are only marginally longer than those in **1**. However, due to the increased steric presence of the neopentyl anion, uranium is located further from the NON-donor plane in complex **2** (0.84 and 0.87 Å versus 0.64 and 0.65 Å in **1**), and the neutral oxygen donor is located further (1.23 and 1.29 Å versus 0.92 and 0.95 Å in 1) from the NUN-plane. In addition, the ligand backbone deviates further from planarity (the angle between the aromatic rings in the xanthene backbone is 33.4 and 34.2° versus 17.6 and 19.0° in **1**), and the 2,6-diisopropylphenyl groups are more strongly rotated away from the axial alkyl group so as to minimize unfavorable steric interactions; C(33)···C(42) = 8.01 and 8.07 Å and C(30)···C(45) = 4.16 and 4.22 Å (cf. C(33)···C(42) = 7.63 and 7.70 Å and C(30)···C(45) = 4.63 and 4.86 Å in **1**).

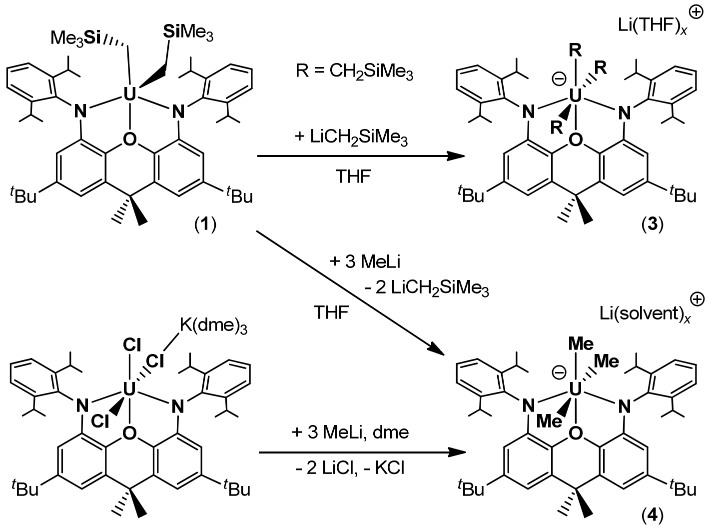
Dialkyl complexes **1** and **2** are thermally stable for days at room temperature in aromatic solvents. However, over the course of several days at 45 °C, **1** and **2** were converted to a mixture of unidentified paramagnetic products with concomitant evolution of $SiMe_4$ or CMe_4, respectively. Upon further heating at 60-80 °C for 24-48 hours, **1** and **2** were fully decomposed to give spectra dominated by $SiMe_4$ or CMe_4 (at this point, ^1H NMR signals attributable to diamagnetic or paramagnetic XA_2 ligand-containing products were low in intensity). We have previously reported similar behaviour for the decomposition of $[(XA_2)Th(CH_2SiMe_3)_2]$ (**1-Th**) at 90 °C.[3]

The reaction to convert **1** to **2** presumably occurs via trialkyl 'ate' intermediates as shown in Scheme 3. These intermediates were not detected in the reaction of **1** with $LiCH_2CMe_3$ in aromatic solvents, and reaction of complex **1** with up to 20 equivalents of $LiCH_2SiMe_3$ in C_6D_6 did not provide any evidence for the formation of $[(XA_2)U(CH_2SiMe_3)_3]^-$ by ^1H NMR spectroscopy. However, trialkyl 'ate' complexes did prove accessible in THF; addition of 1.3 equivalents of $LiCH_2SiMe_3$ to **1** in THF yielded $[Li(THF)_x][(XA_2)U(CH_2SiMe_3)_3]$ (**3**) which was characterized *in-situ* by variable temperature ^1H NMR spectroscopy (Figure 2), and addition of 3.3 equivalents of MeLi to **1** in THF cleanly afforded $[Li(THF)_x][(XA_2)UMe_3]$ (**4**; Scheme 4, Figure S6). Hexane-insoluble $[Li(dme)_3][(XA_2)UMe_3]$ (**4**; Scheme 4) could also be prepared from the reaction of $[(XA_2)UCl_3\{K(dme)_3\}]$ with 3 equivalents of MeLi in dme. By contrast, reactions of **1** or $[(XA_2)UCl_3\{K(dme)_3\}]$ with 2 equivalents of MeLi in dme or THF yielded mixtures of unidentified products. Anionic **3** and **4** are less thermally stable than neutral **1** and **2**, decomposing significantly within hours at room temperature in THF to produce a mixture of unidentified paramagnetic products accompanied by $SiMe_4$ or CH_4, respectively.

Scheme 3. Proposed reaction pathway for the conversion of **1** to **2**.



Scheme 4. Synthesis of complexes **3** and **4**.



The room temperature ^{1}H NMR spectrum of **4** in THF-d_8 is consistent with a top/bottom-symmetric environment (C_{2v} symmetry) on the NMR timescale. Golden-yellow X-ray quality crystals of **4**·dme were obtained from dme/hexanes at –30 °C; the ligand backbone in 6-coordinate **4** (Figure 6) is approximately planar [the angle between the two aryl rings of the xanthene backbone is 6.5°], uranium is located 0.54 Å from the NON-donor plane, the five anionic donors in **4** form a trigonal bipyramid (we are not suggesting that **4** is 5-coordinate) with methyl groups in axial positions, and the neutral donor is located 0.75 Å out of the NUN-plane in the direction of C(50). The U–N distances are approximately 0.1 Å longer than those in complexes **1** and **2**, and only the U–C(48) distance of 2.377(9) Å falls within the range observed for the U–C bonds in **1** and **2**; the U–C(49) and U–C(50) bonds in **4** are substantially longer at 2.493(8) and 2.506(9) Å. The elongated uranium–ligand bond lengths in **4** can be explained on the basis of an increased coordination number at uranium and an overall anionic charge on the complex. The geometry of complex **4** is analogous to that in 6-coordinate [$(XA_2)UCl_3\{K(dme)_3\}$], which also exhibits a planar xanthene backbone and a trigonal bipyramidal arrangement of the anionic donors. However, the U–O and U–N distances in **4** are substantially longer than those in [(XA$_2$)UCl$_3${K(dme)$_3$}] (Table 1), most likely due to decreased Lewis acidity, increased steric hindrance, and complete separation of the anionic portion of the complex from the alkali metal countercation in **4**.

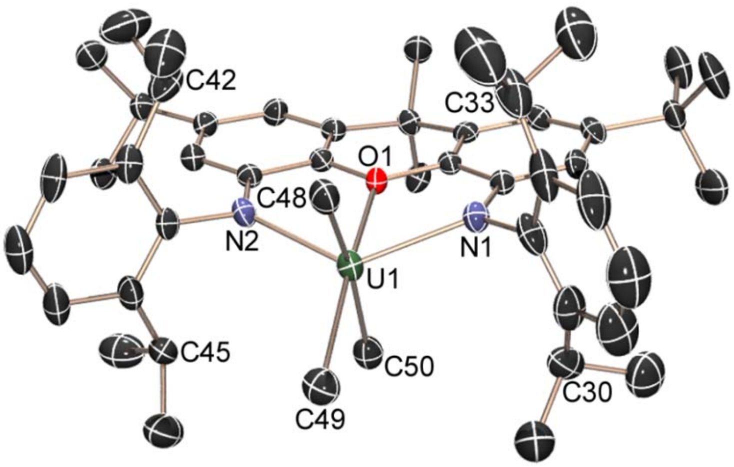


Figure 6. X-Ray crystal structure of [Li(dme)$_3$][(XA$_2$)UMe$_3$]·dme (**4**·dme) with thermal ellipsoids at 30% (collected at 173 K). Hydrogen atoms, dme lattice solvent and the Li(dme)$_3^+$ cation are omitted for clarity.

The extent to which the reactions of **1** with 2.1 equivalents of LiCH$_2$CMe$_3$ (in benzene) or 3.3 equivalents of MeLi (in THF) lie towards the side of the products (**2** or **4** and LiCH$_2$SiMe$_3$) is remarkable and likely[25] reflects the increased basicity of neopentyl and methyl anions compared with the trimethylsilylmethyl anion,[24] leading to stronger uranium–alkyl bonds. The requirement for addition of more than two equivalents of LiCH$_2$CMe$_3$ to convert **1-Th** to **2-Th** is also intriguing in that it highlights distinct differences in the reactivity of thorium and uranium.

Previously reported alkyl exchange reactions at electropositive *d*- or *f*-element centres include: (1) synthesis of [{*o*-C_6H_4(N-Dipp)(PPh(C_6H_4)(=N-Mes))}LuMe$(THF)_2$] by treatment of [{*o*-C_6H_4(N-Dipp)(PPh(C_6H_4)(=N-Mes))}Lu(CH_2SiMe_3)(THF)] with 10 equivalents of $AlMe_3$ in THF,[26] (2) reaction of [Me_2Si(2-Me-$C_9H_5)_2$}YMe(THF)] with $AlEt_3$ followed by addition of THF to yield an approximate 1:1 mixture of the starting methyl complex and [Me_2Si(2-Me-$C_9H_5)_2$}YEt(THF)],[27] and (3) exchange between a growing polymer chain on a d- or f-element polymerization catalyst and the alkyl group of an added trialkylaluminium,[28,29,30,31] trialkylboron,[32] dialkylzinc[30,31,33] or dialkylmagnesium[34] reagent; this mode of reactivity is typically detrimental to olefin polymerization activity,[35] but has found productive use in chain shuttling alkene polymerization[33] and metal-catalyzed “Aufbaureaktion” chemistry.[28,31] Alkyl exchange reactions involving alkyl lithium reactions are more scarce, but have been reported for dialkylmercury compounds in combination with alkyl lithium reagents; these reactions proceed to completion when the alkyl lithium product is insoluble in the solvent employed.[36]

The alkyl exchange reactions in this work also bear resemblance to salt metathesis-like reactions (both alkyl exchange and salt metathesis are classes of transmetallation reaction) involving cyclopentadienyl anion elimination from polar metallocenes. These include the reaction of [$\{Cp^*{}_2U\}_2(\mu\text{-}\eta^6\text{:}\eta^6\text{-}C_6H_6)$] with MX [M = K, X = $N(SiMe_3)_2$ and $OC_6H_2(CMe_3)_2$-2,6-Me-4; M = Li, X = $CH(SiMe_3)_2$ and ^{i}PrNCMeN^{i}Pr] to form [$\{Cp^*XU\}_2(\mu\text{-}\eta^6\text{:}\eta^6\text{-}C_6H_6)$],[37] reaction of [$MnCp_2$] with LiC_2Ph in THF to provide 0.5 [{CpMn(μ-C_2Ph)(THF)}$_2$],[38] reaction of [$MnCp_2$] with 1 or 3 equivalents of Li(hpp) to afford 0.5 [{CpMn(hpp)}$_2$] or [{LiMn$(hpp)_3$}$_2$],[39] reaction of [VCp_2] with 2 equivalents of Li(hpp) to give 0.25 [{$V_2(hpp)_4$}Li(μ-Cp)Li(μ-Cp)Li{$V_2(hpp)_4$}][CpLi(μ-Cp)LiCp],[40] and reaction of [$CrCp_2$] with 2 equivalents of Li(MeNCHNMe) to yield 0.5 [$Cr_2(MeNCHNMe)_4$].[41]

Summary and Conclusions

Preparation and crystallographic characterization of [(XA$_2$)U(CH$_2$SiMe$_3$)$_2$] (**1**), [(XA$_2$)U(CH$_2$CMe$_3$)$_2$] (**2**), and [(XA$_2$)UMe$_3$]$^{-}$ (**4**), and in-situ syntheses of [(XA$_2$)U(CH$_2$SiMe$_3$)$_3$]$^{-}$ (**3**), [(XA$_2$)Th(CH$_2$CMe$_3$)$_2$] (**2-Th**) and [(XA$_2$)Th(CH$_2$SiMe$_3$)(CH$_2$CMe$_3$)] (**5-Th**) are reported. Reaction of **1** with 2.1 equivalents of LiCH$_2$CMe$_3$ in benzene resulted in rapid conversion to **2** and two equivalents of LiCH$_2$SiMe$_3$. This unusual exchange reaction resembles salt metathesis and presumably proceeds via undetected trialkyl 'ate' intermediates. Reactions of this type may find utility for clean in-situ generation of new alkyl complexes, but are only likely to be of preparative value if the solubility of the alkyllithium byproduct permits its complete removal. The generality of this type of alkyl exchange reaction also remains to be determined. However, it is notable that while the reaction of **1** with 2.1 equivalents of LiCH$_2$CMe$_3$ proceeds quantitatively to the dineopentyl complex, the analogous reaction of [(XA$_2$)Th(CH$_2$SiMe$_3$)$_2$] (**1-Th**) requires a significant excess of LiCH$_2$CMe$_3$ to reach completion.

Experimental Section

General Details. General synthetic procedures have been reported elsewhere.[3,16,17,19,42] Deuterated solvents were purchased from ACP chemicals. Neopentyl chloride was purchased from Strem Chemicals. LiCH$_2$SiMe$_3$ (1.0M in *n*-pentane) and MeLi (1.60 M in OEt$_2$) solutions were purchased from Sigma-Aldrich, and prior to use, solid LiCH$_2$SiMe$_3$ and MeLi were obtained by removal of solvent *in vacuo*. H$_2$[XA$_2$],[3] UCl$_4$,[43] [(XA$_2$)UCl$_3${K(dme)$_3$}],[21] [(XA$_2$)Th(CH$_2$SiMe$_3$)$_2$] (**1-Th**),[3] and LiCH$_2$CMe$_3$[44] were prepared using literature procedures. In situ reactions to form **2** (Method 2), **3, 4** (Method 2) and **5-Th** involved the use of small amounts (3.0 to 0.7 mg) of alkyllithium reagents. These reagents were weighed out as accurately as possible using an analytical balance (accurate to 0.1 mg), but the actual reported stoichiometries of these reactions were determined by ^{1}H NMR integration. Sonication was employed in several NMR tube reactions in lieu of stirring. If sonication was continued for extended periods of time, the water in the sonicator was changed periodically (approx. every 30 minutes) to prevent undesired heating of the reaction.

Combustion elemental analyses were performed on a Thermo EA1112 CHNS/O analyzer by Ms. Meghan Fair or Dr. Steve Kornic of this department. X-ray crystallographic analyses were performed on suitable crystals coated in Paratone oil and mounted on a SMART APEX II diffractometer with a 3 kW Sealed tube Mo generator in the McMaster Analytical X-Ray (MAX) Diffraction Facility. Three of four molecules of *n*-hexane in the unit cell of **1**·2(*n*-hexane) (Z = 2), and two molecules of *n*-hexane in the unit cell of **2**·*n*-hexane (Z = 2) were highly disordered and could not be modeled satisfactorily, so were treated using the SQUEEZE routine.[45] ^{1}H, ^{13}C{^{1}H}, DEPT-q, COSY, HSQC and HMBC NMR spectroscopy was performed on Bruker AV-200, DRX-500, and AV-600 spectrometers. All ^{1}H NMR spectra were referenced relative to $SiMe_4$ through a resonance of the employed deuterated solvent or proteo impurity of the solvent; C_6D_6 (7.16 ppm), C_7D_8 (7.09, 7.01, 6.97, 2.08 ppm), and THF-d_8 (3.58, 1.73 ppm) for ^{1}H NMR, and C_6D_6 (128.0 ppm), C_7D_8 (137.48, 128.87, 127.96, 125.13, 20.43 ppm), and THF-d_8 (67.57, 25.37 ppm) for ^{13}C NMR.

All NMR spectra were obtained at room temperature unless otherwise specified. Herein, *Aryl* = 2,6-diisopropylphenyl, and the numbering scheme ($CH^{1,8}$, $C^{2,7}$, $CH^{3,6}$, $C^{4,5}$, $C^{10/13}$ and $C^{11,12}$) for the xanthene ligand backbone is shown in Scheme 1. Most peaks in the ^{1}H NMR spectra of paramagnetic uranium(IV) complexes could be assigned based on integration. The *para*-aryl, $CH^{1,8}$, $CH^{3,6}$ and *tert*-butyl signals were also readily identified since they are unaffected by the presence/absence of top-bottom symmetry on the NMR timescale. Furthermore, the *para*-Ar signal always appeared as a triplet at room temperature, allowing definite assignment. The broad signals integrating to 2H and shifted to particularly low frequency in the spectra of **1** and **2** were speculatively assigned as the isopropyl methine protons (rather than the *meta*-aryl protons), given their close proximity to the paramagnetic U(IV) centre.

$[(XA_2)U(CH_2SiMe_3)_2]$ (1). A mixture of $[(XA_2UCl_3\{K(dme)_3\}]$ (0.150 g, 0.11 mmol) and $LiCH_2SiMe_3$ (0.022 g, 0.24 mmol) in hexanes (20 mL) was stirred at –78 °C and then allowed to warm slowly to room temperature; stirring was continued for a total of 12 hours. The orange-red solution was evaporated to dryness *in vacuo*, and the solid residue was extracted with minimal hexanes. The suspension was centrifuged to remove insoluble KCl and LiCl, and the red mother liquors were cooled to –30 °C. After a few days, X-ray quality bright red crystals of **1**·2(*n*-hexane) were collected in two batches and dried *in vacuo* to provide 0.079 g of **1** (0.072 mmol, 64% yield). Alternatively, crystallization from minimal *n*-pentane at –30 °C followed by drying *in vacuo* provided **1**·*n*-pentane in comparable yield. **^{1}H NMR (C_6D_6, 200 MHz, 298K):** δ 12.30, 7.32 (broad s, 2 × 2H, $CH^{1,8}$ & $CH^{3,6}$), 7.25 (t, $^3J_{H,H}$ 8 Hz, 2H, Aryl-*para*), 2.82 (s, 18H, CMe_3). **^{1}H NMR (toluene-d_8, 500.1 MHz, 298K):** δ 11.41, 8.27 (broad s, 2 × 2H, $CH^{1,8}$ & $CH^{3,6}$), 7.56 (t, $^3J_{H,H}$ 9.3 Hz, 2H, Aryl-*para*), 2.87 (s, 18H, CMe_3). UCH_2 protons were not observed at room temperature. **^{1}H NMR (toluene-d_8, 500.1 MHz, 213K):** δ 178.2, –222.3 (extremely broad s, 2 × 2H, UCH_2), 25.00, 13.51 (broad s, 2 × 3H, CMe_2), 17.93, 4.71 (broad s, 2 × 2H, $CH^{1,8}$ & $CH^{3,6}$), 17.69, –2.08 (broad s, 2 × 9H, $SiMe_3$), 6.45 (broad s, 2H, Aryl-*para*), 5.54, 1.33 (broad s, 2 ×

2H, Aryl-*meta*), 3.40 (s, 18H, CMe_3), –3.14, –14.47, –16.61, –26.85 (broad s, 4 × 6H, $CH\mathit{Me}_2$), –29.86, –96.02 (v. broad s, 2 × 2H, $C\mathit{H}Me_2$). **Anal. Calcd for $C_{55}H_{84}N_2OSi_2U$:** C, 60.97; H, 7.81; N, 2.59%. Found: C, 61.05; H, 8.06; N, 2.38%.

$[(XA_2)U(CH_2CMe_3)_2]$ (2). Method 1. A mixture of $[(XA_2UCl_3\{K(dme)_3\}]$ (0.250 g, 0.19 mmol) and $LiCH_2CMe_3$ (0.031 g, 0.39 mmol) in hexanes (25 mL) was stirred at –78 °C and then allowed to warm slowly to room temperature; stirring was continued for a total of 12 hours. The deep red solution was evaporated to dryness *in vacuo*, and the solid residue was extracted with minimal *n*-pentane. The suspension was centrifuged to remove insoluble KCl and LiCl, and the deep red mother liquors were cooled to –30 °C. After a few days, deep red crystals were collected in two batches and dried *in vacuo* to provide 0.146 g of **2**·*n*-pentane (0.13 mmol, 69% yield). Alternatively, crystallization from minimal hexanes at –30 °C provided X-ray quality crystals of **2**·*n*-hexane in comparable yield. **Method 2.** Complex **2** was generated *in situ* by reaction of **1**·*n*-pentane (0.015 g, 0.013 mmol) with 2.1 equivalents $LiCH_2CMe_3$ (0.0021 g, 0.027 mmol) in C_6D_6. After approximately 1 hour of sonication, ^1H NMR indicated complete conversion of **1** to **2** (the reaction was usually complete after 20 minutes) with concomitant release of $LiCH_2SiMe_3$. Method 2 was not pursued as a means to isolate pure **2**, since both **2** and $LiCH_2SiMe_3$ are highly soluble in hexanes. **^1H NMR (C_6D_6, 500.1 MHz, 298K):** δ 141.1, -142.1 (extremely broad s, 2 x 2H, $UC\mathit{H}_2$) 20.02, –2.43 (v. broad s, 2 × 9H, $CH_2C\mathit{Me}_3$), 17.51, 10.17 (v. broad s, 2 × 3H, CMe_2), 14.71, 4.05 (s, 2 × 2H, $CH^{1,8}$ & $CH^{3,6}$), 5.57 (t, $^3J_{H,H}$ 8 Hz, 2H, Aryl-*para*), 4.42, 2.02 (v. broad s, 2 × 2H, Aryl-*meta*), 2.61 (s, 18H, CMe_3), –3.89, –9.21, –18.84 (v. broad s, 4 × 6H, $CH\mathit{Me}_2$), –27.15, –49.21 (v. broad s, 2 × 2H, $C\mathit{H}Me_2$). **^1H NMR (toluene-d_8, 500.1 MHz, 298K):** δ 134.5, –138.8 (extremely broad s, 2 × 2H, $UC\mathit{H}_2$), 18.78, –2.77 (v. broad s, 2 × 9H, $CH_2C\mathit{Me}_3$), 16.66, 9.80 (v. broad s, 2 × 3H, CMe_2), 14.26, 4.63 (s, 2 × 2H, $CH^{1,8}$ &

$CH^{3,6}$), 5.71 (t, $^{3}J_{H,H}$ 8.6 Hz, 2H, Aryl-*para*), 4.88, 2.29 (v. broad s, 2 × 2H, Aryl-*meta*), 2.66 (s, 18H, CMe_3), –3.43, –8.48, –8.92, –16.73 (v. broad s, 4 × 6H, $CHMe_2$), –24.98, –48.17 (v. broad s, 2 × 2H, $CHMe_2$). **^{1}H NMR (toluene-d_8, 500.1 MHz, 223K):** δ 223.3, –221.5 (extremely broad s, 2 × 2H, UCH_2), 33.64, –2.39 (broad s, 2 × 9H, CH_2CMe_3), 28.61, 15.47 (broad s, 2 × 3H, CMe_2), 20.13, 0.81 (broad s, 2 × 2H, $CH^{1,8}$ & $CH^{3,6}$), 4.45 (broad t, 2H, Aryl-*para*), 3.02 (s, 18H, CMe_3), 1.81, –1.12 (broad s, 2 × 2H, Aryl-*meta*), –7.35, –16.10, –16.48, –25.70 (broad s, 4 × 6H, $CHMe_2$), –46.92, –84.92 (v. broad s, 2 × 2H, $CHMe_2$). **Anal. Calcd for $C_{62}H_{96}N_2OU$:** C, 66.28; H, 8.61; N, 2.49%. Found: C, 66.76; H, 8.01; N, 2.39%.

$[Li(THF)_x][(XA_2)U(CH_2SiMe_3)_3]$ (3) (*in situ*). A mixture of $[(XA_2)U(CH_2SiMe_3)_2]\cdot n$-pentane (**1**·*n*-pentane) (0.010 g, 0.009 mmol) and 1.3 equivalents of $LiCH_2SiMe_3$ (0.0011 g, 0.011 mmol) were taken up in THF-d_8 to afford a yellow solution. Five minutes after mixing, ^{1}H NMR revealed new signals corresponding to **3**, with concomitant loss of **1**. **^{1}H NMR (THF-d_8, 500.1 MHz, 298K):** δ 314.6, 268.8, –161.0 (extremely broad s, 3 × 2H, UCH_2), 35.08, 23.20, –14.20 (v. broad s, 3 × 9H, CH_2SiMe_3), 28.34, –9.54, –11.39, –24.50 (v. broad s, 4 × 6H, $CHMe_2$), 5.85, –12.40 (v. broad s, 2 × 2H, Aryl-*meta*), 4.70, –9.50 (v. broad s, 2 × 3H, CMe_2), 0.19 (t, $^{3}J_{H,H}$ 7 Hz, 2H, Aryl-*para*), –1.49, –28.03 (s, 2 × 2H, $CH^{1,8}$ & $CH^{3,6}$), –1.65, –56.37 (v. broad s, 2 × 2H, $CHMe_2$), –5.34 (s, 18H, CMe_3). **^{1}H NMR (THF-d_8, 500.1 MHz, 223K):** δ 451.0, 378.0, –236.9 (extremely broad s, 3 × 2H, UCH_2), 49.48, 30.58, –21.27 (broad s, 3 × 9H, CH_2SiMe_3), 39.69, –12.53, –13.32, –30.85 (broad s, 4 × 6H, $CHMe_2$), 5.68, –13.68 (broad s, 2 × 3H, CMe_2), 4.07, –20.03 (broad s, 2 × 2H, Aryl-*meta*), –0.86, –60.16 (v. broad s, 2 × 2H, $CHMe_2$), –3.37 (broad s, 2H, Aryl-*para*), –5.28, –40.72 (broad s, 2 × 2H, $CH^{1,8}$ & $CH^{3,6}$), –8.04 (s, 18H, CMe_3).

$[Li(dme)_3][(XA_2)UMe_3]$ (4). Method 1. A mixture of $[(XA_2UCl_3\{K(dme)_3\}]$ (0.150 g, 0.11 mmol) and MeLi (0.008 g, 0.37 mmol) in dme (20 mL) was stirred at –78 °C and then allowed to warm slowly to room temperature; stirring was continued for a total of 12 hours. The yellow solution was evaporated to dryness *in vacuo*, and the solid residue was extracted with toluene (20 mL). The suspension was filtered to remove insoluble KCl and LiCl, and the yellow filtrate was evaporated to dryness *in vacuo*. The solid residue was taken up in minimal dme and layered with hexanes. After a few days at –30 °C, X-ray quality crystals of **4**·dme were obtained and dried *in vacuo* to provide 0.046 g of **4**·dme (0.035 mmol, 31% yield). The low yield likely results from losses during extraction as a consequence of poor solubility in toluene. **Method 2.** Complex **4** can be prepared cleanly *in situ* by reaction of **1**·*n*-pentane (0.010 g, 0.009 mmol) and MeLi (0.0007 g, 0.03 mmol) in THF-d_8 to afford a yellow solution. After 30 minutes of sonication, ^{1}H NMR revealed new signals corresponding to **4** with concomitant loss of **1**. **^{1}H NMR (THF-d_8, 500.1 MHz, 298K):** δ 6.29, –7.04 (broad s, 2 × 12H, CH*Me*$_2$), –1.53 (t, $^3J_{H,H}$ 6 Hz, 2H, Aryl-*para*), –2.26 (s, 6H, CMe$_2$), –2.44, –28.86 (s, 2 × 2H, CH^{1,8} & CH^{3,6}), –4.59 (v. broad s, 4H, C*H*Me$_2$), –5.69 (s, 18H, CMe$_3$), –5.84 (d, $^3J_{H,H}$ 5 Hz, 4H, Aryl-*meta*). Signals corresponding to the UC*H*$_3$ protons were not located between +400 to –400 ppm. **Anal. Calcd for $C_{62}H_{101}N_2O_7LiU$ prepared using method 1:** C, 60.47; H, 8.27; N, 2.27%. Found: C, 60.79; H, 7.73; N, 2.08%.

[(XA$_2$)Th(CH$_2$CMe$_3$)$_2$] (2-Th) (*in situ*). A mixture of [(XA$_2$)Th(CH$_2$SiMe$_3$)$_2$]·{O(SiMe$_3$)$_2$}$_{0.5}$ (**1-Th**·{O(SiMe$_3$)$_2$}$_{0.5}$) (0.020 g, 0.017 mmol) and 15 equivalents of LiCH$_2$CMe$_3$ (0.022 g, 0.26 mmol) were taken up in toluene-d_8 to afford a colourless solution. Five minutes after mixing, ^{1}H NMR revealed new signals corresponding to **2-Th** and free LiCH$_2$SiMe$_3$, with concomitant loss of **1-Th**. **^{1}H NMR (toluene-d_8, 600.1 MHz, 298 K):** δ 7.25 (broad s, 6H, Aryl-*meta* & Aryl-*para*), 6.76, 6.03 (d, $^4J_{H,H}$ 2 Hz, 2 × 2H, CH^{1,8} & CH^{3,6}), 3.63 (v. broad s, 4H, C*H*Me$_2$), 1.66 (s, 6H, CMe$_2$), 1.41, 1.15 (broad s, 2 × 12H, CH*Me*$_2$), 1.32 (broad s, 4H, ThC*H*$_2$), 1.18 (s, 18H, CMe$_3$), 0.90 (broad s, 18H, ThCH$_2$C*Me*$_3$). **^{1}H NMR (toluene-*d*$_8$, 500.1 MHz, 213 K):** *δ* 7.28 (m, $^3J_{\mathrm{H,H}}$ 7 Hz, 4H, Aryl-*meta* & Aryl-*para*), 7.16 (d, $^3J_{\mathrm{H,H}}$ 7 Hz, 2H, Aryl-*meta*), 6.79, 6.14 (s, 2 × 2H, CH^{1,8} & CH^{3,6}), 4.19, 3.20 (broad sept, $^3J_{\mathrm{H,H}}$ 6.3 Hz, 2 × 2H, C*H*Me$_2$), 1.74, 1.54 (broad s, 2 × 3H, CMe$_2$), 1.60, 1.36, 1.22, 1.10 (broad d, $^3J_{\mathrm{H,H}}$ 6.2 Hz, 4 × 6H, CH*Me*$_2$), 1.29, 0.71 (broad s, 2 × 9H, ThCH$_2$C*Me*$_3$), 1.17 (broad s, 18H, CMe$_3$) 0.97, –0.30 (broad s, 2 × 2H, ThC*H*$_2$CMe$_3$). **^{13}C{^{1}H} NMR (toluene-*d*$_8$, 150 MHz, 298 K):** *δ* 148.14 (*C*^{2,7}), 147.86 (Aryl-*C*$_{ortho}$), 146.24 (*C*^{4,5}), 141.93 (*C*^{11,12}), 136.32 (Aryl-*C*$_{ipso}$), 130.02 (*C*^{10,13}), 128.04 (Aryl-*C*$_{para}$), 125.38 (Aryl-*C*$_{meta}$), 110.56, 109.89 (*C*H^{1,8} & *C*H^{3,6}), 37.94 (ThCH$_2$*C*Me$_3$), 35.66 (ThCH$_2$C*Me*$_3$), 35.24 (*C*Me$_2$), 35.03 (*C*Me$_3$), 31.67 (C*Me*$_3$), 29.0 (*C*HMe$_2$), 26.25, 25.17 (CH*Me*$_2$). **^{13}C{^{1}H} NMR (toluene-*d*$_8$, 150 MHz, 213 K):** *δ* 147.96, 147.32 (2 × Aryl-*C*$_{ortho}$), 147.78 (*C*^{2,7}), 146.06 (*C*^{4,5}), 142.24 (*C*^{11,12}), 135.81, 120.59 (2 × Th*C*H$_2$CMe$_3$), 135.02 (Aryl-*C*$_{ipso}$), 129.91 (*C*^{10,13}), 128.18, 125.40 (Aryl-*C*$_{para}$ & Aryl-*C*$_{meta}$), 110.33, 109.37 (*C*H^{1,8} & *C*H^{3,6}), 39.11, 36.37 (2 × ThCH$_2$*C*Me$_3$), 36.05, 23.96 (2 × C*Me*$_2$), 35.97, 35.35 (2 × ThCH$_2$C*Me*$_3$), 35.13 (*C*Me$_2$), 34.90 (*C*Me$_3$), 31.43 (C*Me*$_3$), 29.44, 28.08 (2 × *C*HMe$_2$), 27.03, 25.77, 25.36, 24.33 (4 × CH*Me*$_2$).

[(XA$_2$)Th(CH$_2$SiMe$_3$)(CH$_2$CMe$_3$)] (5-Th) (*in situ*). A mixture of [(XA$_2$)Th(CH$_2$SiMe$_3$)$_2$]·0.5{O(SiMe$_3$)$_2$} (**1-Th**·0.5{O(SiMe$_3$)$_2$}) (0.020 g, 0.017 mmol) and 2.2 equivalents of LiCH$_2$CMe$_3$ (0.0030 g, 0.04 mmol) were taken up in toluene-*d*$_8$ to afford a colourless solution. Five minutes after mixing, ^{1}H NMR revealed new signals corresponding to an approximate 1:1:3:1 mixture of **5-Th**, **2-Th**, free LiCH$_2$SiMe$_3$, and remaining LiCH$_2$CMe$_3$, with concomitant loss of **1-Th**. **^{1}H NMR of 5-Th (toluene-*d*$_8$, 600.1 MHz, 298 K):** *δ* 7.29, 7.21 (dd, $^3J_{\mathrm{H,H}}$ 7.7 Hz; $^4J_{\mathrm{H,H}}$ 1.7 Hz, 2 × 2H, Aryl-*meta*), 7.26 (t, $^3J_{\mathrm{H,H}}$ 7.7 Hz, 2H, Aryl-*para*), 6.77, 6.04 (d, $^4J_{\mathrm{H,H}}$ 2 Hz, 2 × 2H, CH^{1,8} & CH^{3,6}), 3.83, 3.32 (broad sept, $^3J_{\mathrm{H,H}}$ 7 Hz, 2 × 2H, C*H*Me$_2$), 1.70, 1.64 (s, 2 × 3H, CMe$_2$), 1.50, 1.32, 1.25, 1.08 (d, $^3J_{\mathrm{H,H}}$ 7 Hz, 4 × 6H, CH*Me*$_2$), 1.19 (s, 18H, CMe$_3$), 0.74 (s, 9H, ThCH$_2$C*Me*$_3$), 0.21 (broad s, 2H, ThC*H*$_2$CMe$_3$), 0.05 (s, 9H, ThCH$_2$Si*Me*$_3$), –0.11 (broad s, 2H, ThC*H*$_2$SiMe$_3$). **^{13}C{^{1}H} NMR of 5-Th (toluene-d_8, 150 MHz, 298 K):** δ 148.36, 147.86 (2 × Aryl-C_{ortho}), 148.23 ($C^{2,7}$), 145.92 ($C^{4,5}$), 142.0 ($C^{11,12}$), 135.66 (Aryl-C_{ipso}), 129.79 ($C^{10,13}$), 128.26 (Aryl-C_{para}), 125.55, 125.48 (2 × Aryl-C_{meta}), 110.49, 110.19 (CH^{1,8} & CH^{3,6}), 37.44 (ThCH$_2$*C*Me$_3$), 35.54 (ThCH$_2$C*Me*$_3$), 35.26 (*C*Me$_2$), 35.12 (*C*Me$_3$), 33.87, 28.33 (2 × C*Me*$_2$), 31.63 (C*Me*$_3$), 29.43, 28.47 (2 × *C*HMe$_2$), 26.92, 25.91, 25.46, 24.77 (4 × CH*Me*$_2$), 3.48 (ThCH$_2$Si*Me*$_3$).

ASSOCIATED CONTENT

Supporting Information. ^{1}H NMR spectra of **1** (variable temperature), **3** (variable temperatue), **4**, **1-Th**, **2-Th** and **5-Th** and CIF files for **1**, **2** and **4** are available free of charge *via* the internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

* Phone: 905-525-9140, Fax: 905-522-2509. E-mail: emslied@mcmaster.ca.

ACKNOWLEDGMENT

D.J.H.E. thanks NSERC of Canada for a Discovery Grant and N.R.A. thanks the Government of Ontario for an Ontario Graduate Scholarship (OGS) and McMaster University for a Richard Fuller Memorial Scholarship.

REFERENCES

(1) Burns, C. J.; Neu, M. P.; Boukhalfa, H.; Gutowski, K. E.; Bridges, N. J.; Rogers, R. D., Chapter 3.3: The Actinides. In *Comprehensive Coordination Chemistry II*, Parkin, G. F. R., Ed.; Elsevier Ltd.: San Diego, 2004; Vol. 3, p 189.

(2) Fox, A. R.; Bart, S. C.; Meyer, K.; Cummins, C. C. *Nature* **2008**, *455*, 341.

(3) Cruz, C. A.; Emslie, D. J. H.; Harrington, L. E.; Britten, J. F.; Robertson, C. M. *Organometallics* **2007**, *26*, 692.

(4) (a) Fortier, S.; Melot, B. C.; Wu, G.; Hayton, T. W. *J. Am. Chem. Soc.* **2009**, *131*, 15512. (b) Fortier, S.; Walensky, J. R.; Wu, G.; Hayton, T. W. *J. Am. Chem. Soc.* **2011**, *133*, 11732.

(5) Duhović, S.; Khan, S.; Diaconescu, P. L. *Chem. Commun.* **2010**, *46*, 3390.

(6) Kraft, S. J.; Fanwick, P. E.; Bart, S. C. *J. Am. Chem. Soc.* **2012**, *134*, 6160.

(7) Seaman, L. A.; Walensky, J. R.; Wu, G.; Hayton, T. W. *Inorg. Chem.* **2012**, asap.

(8) (a) Takats, J., Organoactinide Complexes Containing Classical Ligands. In *Fundamental and Technological Aspects of Organo-f-Element Chemistry*, Nato Science Series C: *Vol. 155*, (b) Marks, T. J.; Fragalà, I. L., Eds.; D. Reidel Publishing Company: Dordrecht, 1985; p 159. (c) Marks, T. J.; Day, V. W., Actinide Hydrocarbyl and Hydride Chemistry. In *Fundamental and Technological Aspects of Organo-f-Element Chemistry*, Nato Science Series C: *Vol. 155*, Marks, T. J.; Fragalà, I. L., Eds.; D. Reidel Publishing Company: Dordrecht, 1985; p 115. (d) Burns, C. J.; Clark, D. L.; Sattelberger, A. P., Actinides: Organometallic Chemistry. In *Encyclopedia of Inorganic Chemistry*, King, R. B.; Lukehart, C. M., Eds.; John Wiley & Sons: Chichester, England, 2005; Vol. 1, p 33.

(9) Only terminal alkyl complexes are included in Figure 1. Metallated ligand complexes or complexes of ylide, aryl, alkynyl or π-allyl ligands are not included.

(10) Campello, M. P. C.; Calhorda, M. J.; Domingos, Â.; Galvão, A.; Leal, J. P.; de Matos, A. P.; Santos, I. *J. Organomet. Chem.* **1997**, *538*, 223.

(11) (a) Silva, M.; Marques, N.; de Matos, A. P. *J. Organomet. Chem.* **1995**, *493*, 129. (b) Domingos, Â.; Marques, N.; de Matos, A. P.; Santos, I.; Silva, M. *Organometallics* **1994**, *13*, 654. (c) Matson, E. M.; Forrest, W. P.; Fanwick, P. E.; Bart, S. C. *J. Am. Chem. Soc.* **2011**, *133*, 4948. (d) Matson, E. M.; Forrest, W. P.; Fanwick, P. E.; Bart, S. C. *Organometallics* **2012**, *31*, 4467.

(12) Campello, M. P. C.; Domingos, Â.; Galvao, A.; de Matos, A. P.; Santos, I. *J. Organomet. Chem.* **1999**, *579*, 5.

(13) Wedler, M.; Knösel, F.; Edelmann, F. T.; Behrens, U. *Chem. Ber.* **1992**, *125*, 1313.

(14) Jantunen, K. C.; Batchelor, R. J.; Leznoff, D. B. *Organometallics* **2004**, *23*, 2186.

(15) (a) Jantunen, K. C.; Haftbaradaran, F.; Katz, M. J.; Batchelor, R. J.; Schatte, G.; Leznoff, D. B. *Dalton Trans.* **2005**, 3083. (b) Hayes, C. E.; Leznoff, D. B. *Organometallics* **2010**, *29*, 767. (c) Hayes, C. E.; Platel, R. H.; Schafer, L. L.; Leznoff, D. B. *Organometallics* **2012**, *31*, 6732.

(16) Cruz, C. A.; Emslie, D. J. H.; Jenkins, H. A.; Britten, J. F. *Dalton Trans.* **2010**, *39*, 6626.

(17) Cruz, C. A.; Emslie, D. J. H.; Robertson, C. M.; Harrington, L. E.; Jenkins, H. A.; Britten, J. F. *Organometallics* **2009**, *28*, 1891.

(18) (a) Monreal, M. J.; Diaconescu, P. L. *Organometallics* **2008**, *27*, 1702. (b) Duhovic, S.; Monreal, M. J.; Diaconescu, P. L. *J. Organomet. Chem.* **2010**, *695*, 2822.

(19) Cruz, C. A.; Emslie, D. J. H.; Harrington, L. E.; Britten, J. F. *Organometallics* **2008**, *27*, 15.

(20) Korobkov, I.; Gambarotta, S.; Yap, G. P. A. *Angew. Chem. Int. Ed.* **2003**, *42*, 814.

(21) B. Vidjayacoumar; S. Ilango; M. J. Ray; T. Chu; K. B. Kolpin; N. R. Andreychuk; C. A. Cruz; D. J. H. Emslie; H. A. Jenkins; Britten, J. F. *Dalton Trans.* **2012**, *41*, 8175.

(22) In **1-Th**, α-agostic interactions were confirmed by small $^{1}J_{13C,1H}$ coupling constants for the ThCH_2 groups. The An–CH_2–$SiMe_3$ angles in **1-Th** were 126.8(3) and 127.6(3)°. In paramagnetic **1** and **2**, $^{1}J_{13C,1H}$ coupling constants could not be measured, so it is not possible to draw any definite conclusions from the expanded U–C–E (E = Si and C) angles.

(23) Shannon, R. D. *Acta Cryst.* **1976**, *A32*, 751.

(24) (a) Wetzel, D. M.; Brauman, J. I. *J. Am. Chem. Soc.* **1988**, *110*, 8333. (b) Damrauer, R.; Kass, S. R.; Depuy, C. H. *Organometallics* **1988**, *7*, 637.

(25) The thermodynamic driving force for conversion of **1** to **2** and **4** could alternatively be related to different levels of aggregation for the $LiCH_2CMe_3$ and MeLi reactants versus the $LiCH_2SiMe_3$ product in solution. However, this explanation seems unlikely given that the reaction to form **2** was performed in an aromatic solvent while the reaction to form **4** was performed in THF, and the extent of alkyl lithium aggregation in THF can be expected to be significantly less than that in benzene or toluene.

(26) Liu, B.; Liu, X. L.; Cui, D. M.; Liu, L. *Organometallics* **2009**, *28*, 1453.

(27) Klimpel, M. G.; Eppinger, J.; Sirsch, P.; Scherer, W.; Anwander, R. *Organometallics* **2002**, *21*, 4021.

(28) Mani, G.; Gabbai, F. P. *Angew. Chem. Int. Ed.* **2004**, *43*, 2263.

(29) (a) Samsel, E. G; Eisenberg, D. C. (Ethyl Corporation, USA), US Patent 5,276,220, 1994. (b) Kretschmer, W. P.; Bauer, T.; Hessen, B.; Kempe, R. *Dalton Trans.* **2010**, *39*, 6847. (c) Kretschmer, W. P.; Meetsma, A.; Hessen, B.; Schmalz, T.; Qayyum, S.; Kempe, R. *Chem. Eur. J.* **2006**, *12*, 8969. (d) Hey, T. W.; Wass, D. F. *Organometallics* **2010**, *29*, 3676.

(30) Ni Bhriain, N.; Brintzinger, H. H.; Ruchatz, D.; Fink, G. *Macromolecules* **2005**, *38*, 2056.

(31) Wei, J.; Zhang, W.; Sita, L. R. *Angew. Chem. Int. Ed.* **2010**, *49*, 1768.

(32) Lin, W. T.; Niu, H.; Chung, T. C. M.; Dong, J. Y. *J. Polym. Sci. Pol. Chem.* **2010**, *48*, 3534.

(33) Arriola, D. J.; Carnahan, E. M.; Hustad, P. D.; Kuhlman, R. L.; Wenzel, T. T. *Science* **2006**, *312*, 714.

(34) Pelletier, J. F.; Mortreux, A.; Olonde, X.; Bujadoux, K. *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1854.

(35) (a) Hartwig, J. F., *Organotransition Metal Chemistry: From Bonding to Catalysis*, University Science Books: Sausalito, California, 2010. (b) Crabtree, R. H., *The Organometallic Chemistry of the Transition Metals*, 3rd ed.; John Wiley & Sons: Toronto, 2001.

(36) (a) Schlenk, W.; Holtz, J. *Chem. Ber.* **1917**, 262. (b) Zieger, H.; Perri, C.; Bharucha, K. *Tetrahedron Lett.* **1987**, *28*, 5989.

(37) Evans, W. J.; Traina, C. A.; Ziller, J. W. *J. Am. Chem. Soc.* **2009**, *131*, 17473.

(38) Alvarez, C. S.; Boss, S. R.; Burley, J. C.; Humphry, S. M.; Layfield, R. A.; Kowenicki, R. A.; McPartlin, M.; Rawson, J. M.; Wheatley, A. E. H.; Wood, P. T.; Wright, D. S. *Dalton Trans.* **2004**, 3481.

(39) Brinkmann, C.; Garcia, F.; Morey, J. V.; McPartlin, M.; Singh, S.; Wheatley, A. E. H.; Wright, D. S. *Dalton Trans.* **2007**, 1570.

(40) Fernandez-Cortabitarte, C.; Garcia, F.; Morey, J. V.; McPartlin, M.; Singh, S.; Wheatley, A. E. H.; Wright, D. S. *Angew. Chem. Int. Ed.* **2007**, *46*, 5425.

(41) Haywood, J.; Stokes, F. A.; Less, R. J.; McPartlin, M.; Wheatley, A. E. H.; Wright, D. S. *Chem. Commun.* **2011**, *47*, 4120.

(42) Cruz, C. A.; Chu, T.; Emslie, D. J. H.; Jenkins, H. A.; Harrington, L. E.; Britten, J. F. *J. Organomet. Chem.* **2010**, *695*, 2798.

(43) Kiplinger, J. L.; Morris, D. E.; Scott, B. L.; Burns, C. J. *Organometallics* **2002**, *21*, 5978.

(44) Schrock, R. R.; Fellmann, J. D. *J. Am. Chem. Soc.* **1978**, *100*, 3359.

(45) Sluis, P. V. D.; Spek, A. L. *Acta Crystallogr.* **1990**, *A46*, 194.

For Table of Contents Use Only

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

Nicholas R. Andreychuk,† Sougandi Ilango,† Balamurugan Vidjayacoumar,† David J. H. Emslie,*,† and Hilary A. Jenkins‡

TOC Text: The uranium alkyl complex [(XA$_2$)U(CH$_2$SiMe$_3$)$_2$] was prepared, and reaction with 2.1 equivalents of LiCH$_2$CMe$_3$ in benzene or 3.3 equivalents of MeLi in THF yielded [(XA$_2$)U(CH$_2$CMe$_3$)$_2$] and [Li(THF)$_x$][(XA$_2$)UMe$_3$], respectively. These unusual alkyl exchange reactions resemble salt metathesis reactions, but with elimination of an alkyl lithium instead of a lithium halide. The equilibrium in these reactions lies far to the side of the bis-neopentyl and trimethyl uranium products. By contrast, reaction of [(XA$_2$)Th(CH$_2$SiMe$_3$)$_2$] with 2.2 equivalents of LiCH$_2$CMe$_3$ afforded an approximate 1:1:3:1 mixture of [(XA$_2$)Th(CH$_2$CMe$_3$)$_2$], [(XA$_2$)Th(CH$_2$SiMe$_3$)(CH$_2$CMe$_3$)], LiCH$_2$SiMe$_3$ and LiCH$_2$CMe$_3$.

TOC Graphic: