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

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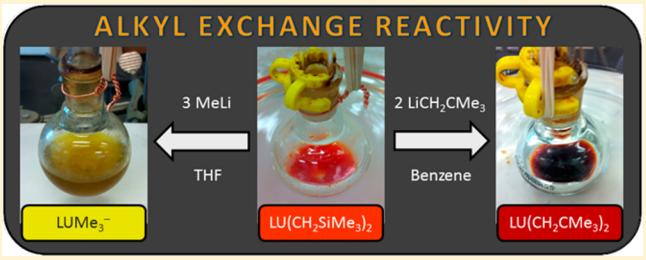
Supporting Information

**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 2 equiv of ((trimethylsilyl)methyl)lithium or neopentyllithium 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 1 equiv 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 3 equiv of methyllithium in dme afforded yellow $[Li(dme)_3][(XA_2)UMe_3]$ (**4**). Reaction of **1** with 2.1 equiv of $LiCH_2CMe_3$ in benzene resulted in rapid conversion to **2**, with release of 2 equiv of $LiCH_2SiMe_3$. Similarly, reaction of **1** with 3.3 equiv of MeLi in THF provided **4** as the $[Li(THF)_x]^+$ salt, accompanied by 2 equiv of $LiCH_2SiMe_3$. These unusual alkyl exchange reactions resemble salt metathesis reactions, but with elimination of an alkyllithium 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**. In contrast, the reaction of $[(XA_2)Th(CH_2SiMe_3)_2]$ (**1-Th**) with 2.2 equiv 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 behavior 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 noncarbocyclic 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.

We have previously employed McConville's BDPP ligand and our own $XA_2$ ligand for the synthesis of neutral thorium(IV) bis((trimethylsilyl)methyl) 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 pre-

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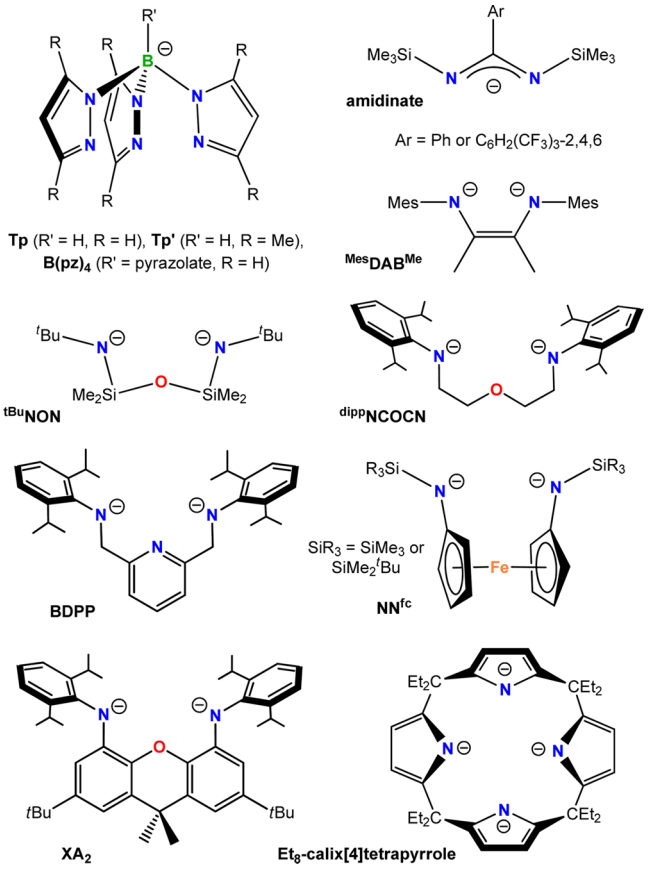



**Figure 1.** Multidentate anionic ligands previously employed in the synthesis of actinide alkyl[9] complexes: (a) Tp,[10] Tp′,[11] and $B(pz)_4$ (pz = pyrazolate);[12] (b) amidinate;[13] (c) $^{Mes}DAB^{Me}$;[6] (d) $^{tBu}NON$;[14,15] (e) $^{dipp}NCOCN$;[15] (f) BDPP;[3,5,16,17] (g) $NN^{fc}$;[5,18] (h) $XA_2$;[3,17,19] (i) $Et_8$-calix[4]tetrapyrrole.[20]

pared 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.

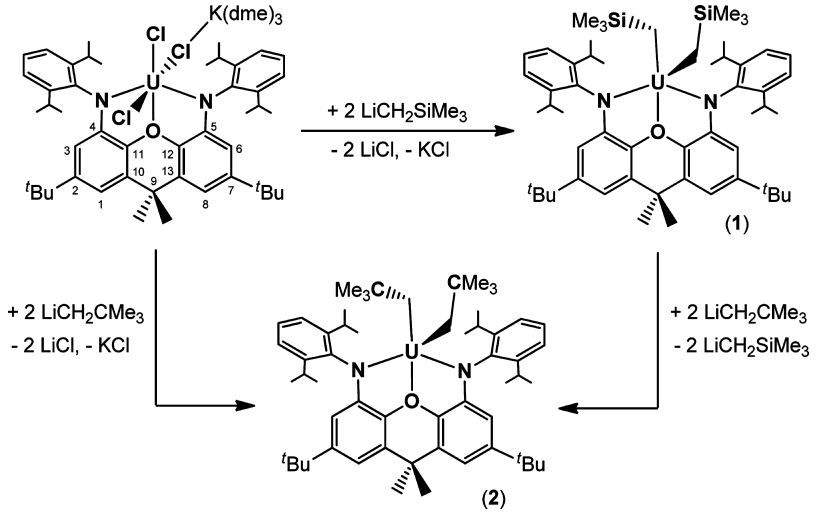
## RESULTS AND DISCUSSION

Reaction of $[(XA_2)UCl_3\{K(dme)_3\}]$ with 2 equiv 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), indicative of $C_s$ symmetry.

The X-ray crystal structure of **1**·2(*n*-hexane) (Figure 3 and Table 1) has two independent but structurally analogous five-coordinate molecules in the unit cell, each with one $CH_2SiMe_3$ 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 four-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 $^1H$ NMR spectra.

The U−C distances of 2.368(7)−2.418(7) Å are comparable with those observed for the other crystallographically characterized neutral uranium(IV) (trimethylsilyl)methyl 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

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





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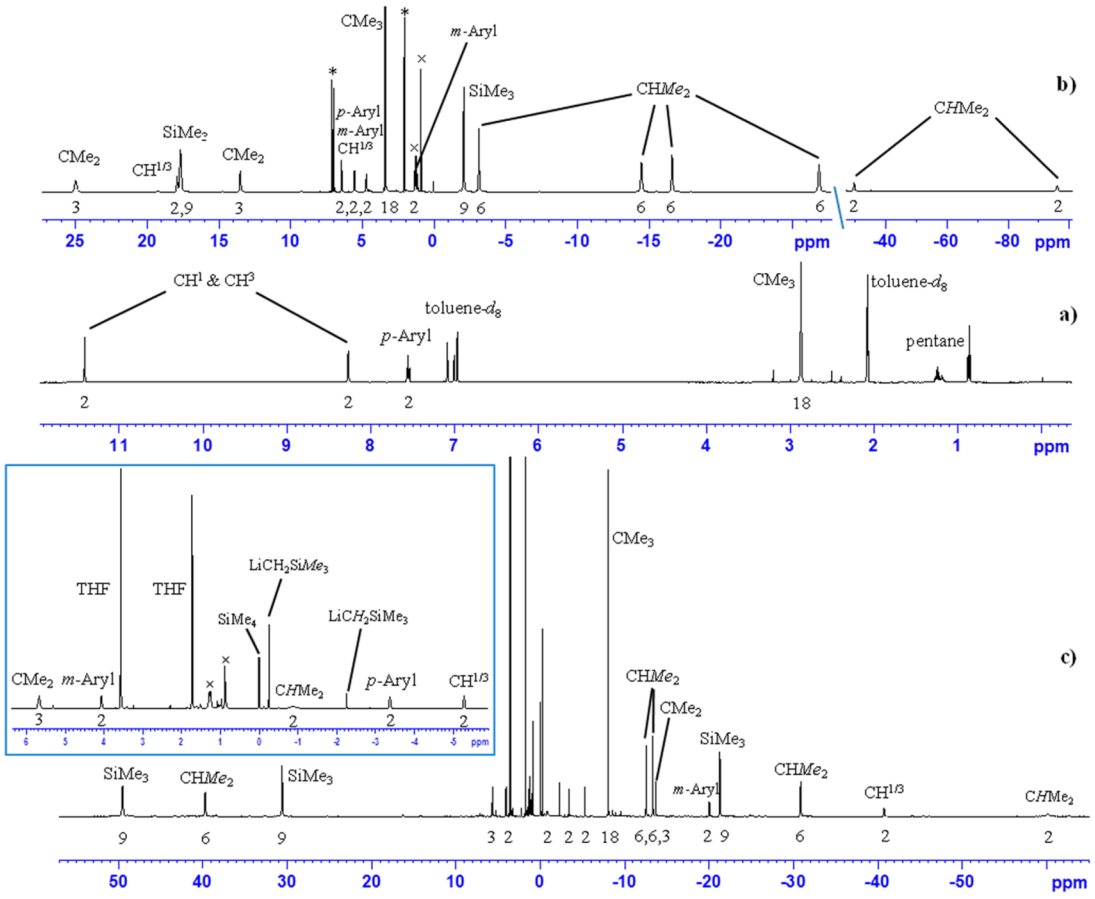


**Figure 2.** $^1$H NMR spectra (500 MHz): (a) $[(XA_2)U(CH_2SiMe_3)_2]$ (**1**) in toluene-$d_8$ at room temperature; (b) complex **1** in toluene-$d_8$ at −60 °C; and (c) in situ generated $[Li(THF)_x][(XA_2)U(CH_2SiMe_3)_3]$ (**3**) in THF-$d_8$ at −50 °C. In the figure, * denotes toluene-$d_8$ and × denotes *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.

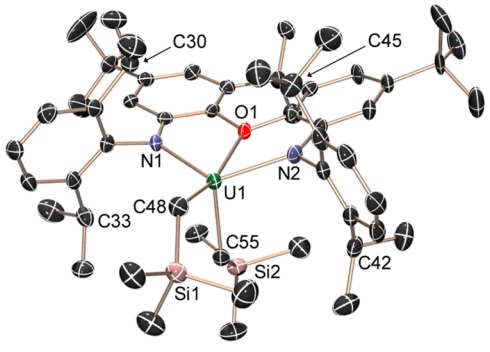


**Figure 3.** X-ray crystal structure of $[(XA_2)U(CH_2SiMe_3)_2]\cdot 2(n\text{-hexane})$ (**1**·2(*n*-hexane)) with thermal ellipsoids at the 30% probability level (collected at 173 K). Only one of the two independent molecules in the unit cell is shown. Hydrogen atoms and hexane solvent are omitted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

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−diaryl ether 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 six-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 angles between the two aryl rings of the xanthene backbone are 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 are 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 equiv 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 2 equiv of $LiCH_2SiMe_3$ (Scheme 1). Treatment of complex **2** with up to 80 equiv of $LiCH_2SiMe_3$ in $C_6D_6$ did not re-form detectable amounts of **1** by $^1$H NMR spectroscopy; thus, the equilibrium in this reaction must lie far to the side of complex **2**. This unusual reaction bears a resemblance to salt metathesis (both


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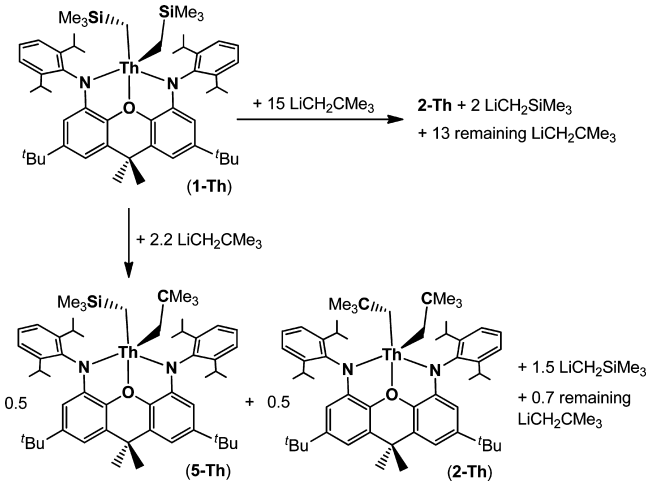
**Table 1. Selected Bond Lengths (Å) and Angles (deg) for $XA_2$ Complexes 1, 2, and 4 as Well as the Previously Reported 1-Th and $[(XA_2)UCl_3\{K(dme)_3\}]$**

| | $(XA_2)Th(CH_2SiMe_3)_2$ (**1-Th**) | $(XA_2)U(CH_2SiMe_3)_2$ (**1**) | $(XA_2)U(CH_2CMe_3)_2$ (**2**) | $(XA_2)UMe_3$ anion (**4**) | $(XA_2)UCl_3K(dme)_3$ |
|---|---|---|---|---|---|
| lattice solvent | toluene | 2 *n*-hexane | *n*-hexane | dme | none |
| ref | 3 | this work | this work | this work | 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−Cl2: 2.620(2), 2.625(2) |
| | | | | U−C50: 2.493(8) | 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) | Cl1−U−Cl2: 89.91(6) |
| | | | | C49−U−C50: 85.7(3) | Cl1−U−Cl3: 88.25(6) |
| | | | | C48−U−C50: 169.9(3) | 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−Cl2: 89.2(1), 92.5(1) |
| | | | | N−U−C50: 90.5(2), 93.3(2) | 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 |

alkyl exchange and salt metathesis are classes of transmetalation reactions), 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 equiv of $LiCH_2CMe_3$ cleanly provided $[(XA_2)Th(CH_2CMe_3)_2]$ (**2-Th**; Figure S5 (Supporting Information)). However, addition of 2.2 equiv of $LiCH_2CMe_3$ to **1-Th** 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 and Figure S4 (Supporting Information)). This product distribution was established within 5 min 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**).

Complex **2** could also be prepared by a traditional salt metathesis reaction between $[(XA_2)UCl_3\{K(dme)_3\}]$ and 2 equiv of $LiCH_2CMe_3$ (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 $^1H$ 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).

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




The solid-state geometry of complex **2** (Figure 5 and 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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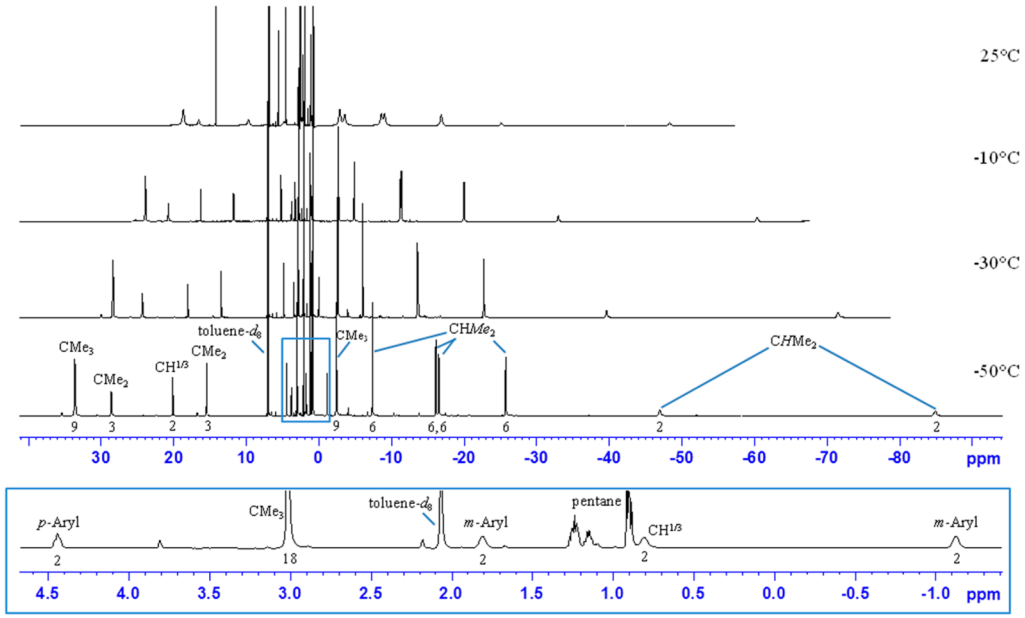



**Figure 4.** 500 MHz $^1$H NMR spectra of $[(XA_2)U(CH_2CMe_3)_2]$ (**2**) in toluene-$d_8$ at temperatures from 25 to −50 °C. Numbers below the baseline indicate the integration of each peak. Signals for U−C$H_2$ protons, which are located at very high (>100 ppm) and very low (<−100 ppm) frequencies, are not shown. The inset at the bottom shows a portion of the −50 °C spectrum.

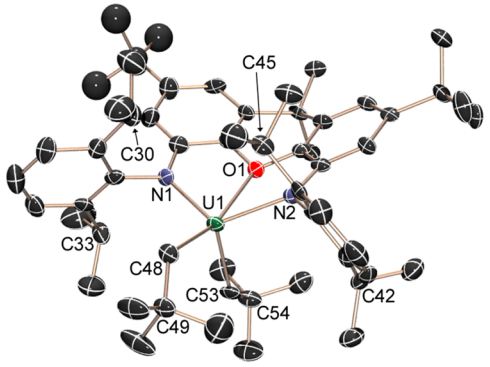


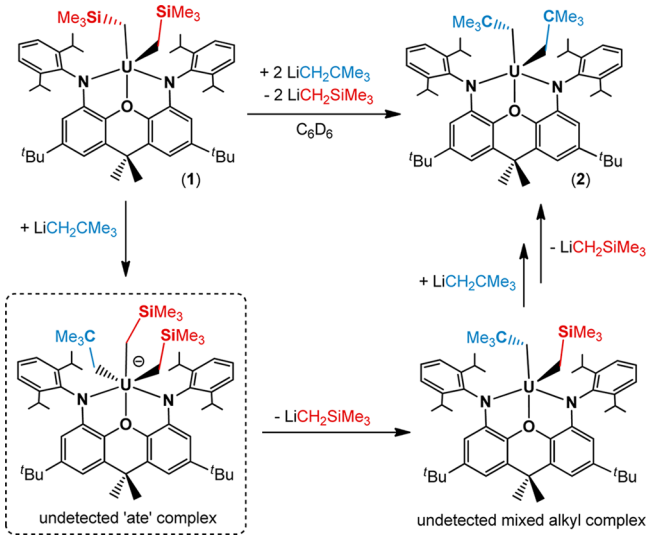

**Figure 5.** X-ray crystal structure of $[(XA_2)U(CH_2CMe_3)_2]\cdot(n\text{-hexane})$ (**2**·(*n*-hexane)) with thermal ellipsoids at the 50% probability level (collected at 100 K). Only one of the two independent molecules in the unit cell is shown. Hydrogen atoms and hexane solvent are omitted for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

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 angles between the aromatic rings in the xanthene backbone are 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 h, **1** and **2** were fully decomposed to give spectra dominated by $SiMe_4$ or $CMe_4$ (at this point, $^1$H NMR signals attributable to diamagnetic or paramagnetic $XA_2$ ligand-containing products were low in intensity). We have previously reported similar behavior 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 equiv 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 $^1$H NMR spectroscopy. However, trialkyl "ate" complexes did prove

**Scheme 3. Proposed Reaction Pathway for the Conversion of 1 to 2**





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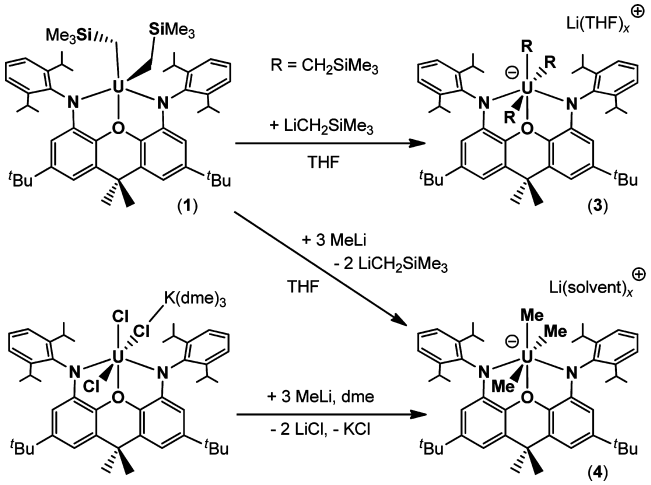
accessible in THF; addition of 1.3 equiv of $LiCH_2SiMe_3$ to **1** in THF yielded $[Li(THF)_x][(XA_2)U(CH_2SiMe_3)_3]$ (**3**), which was characterized in situ by variable-temperature $^1H$ NMR spectroscopy (Figure 2), and addition of 3.3 equiv of MeLi to **1** in THF cleanly afforded $[Li(THF)_x][(XA_2)UMe_3]$ (**4**; Scheme 4 and Figure S6 (Supporting Information)). Hexane-insoluble

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




$[Li(dme)_3][(XA_2)UMe_3]$ (**4**; Scheme 4) could also be prepared from the reaction of $[(XA_2)UCl_3\{K(dme)_3\}]$ with 3 equiv of MeLi in dme. In contrast, reactions of **1** or $[(XA_2)UCl_3\{K(dme)_3\}]$ with 2 equiv 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 over several days at room temperature in THF to produce a mixture of unidentified paramagnetic products accompanied by $SiMe_4$ or $CH_4$, respectively.

The room-temperature $^1H$ NMR spectrum of **4** in THF-$d_8$ is consistent with a top−bottom-symmetric environment ($C_{2v}$ symmetry) on the NMR time scale. Golden yellow X-ray-quality crystals of **4**·dme were obtained from dme/hexanes at −30 °C; the ligand backbone in six-coordinate **4** (Figure 6) is

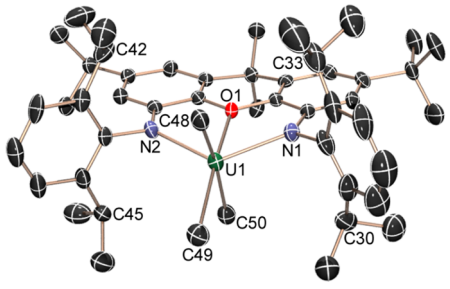



**Figure 6.** X-ray crystal structure of $[Li(dme)_3][(XA_2)UMe_3]$·dme (**4**·dme) with thermal ellipsoids at 30% (collected at 173 K). Hydrogen atoms, dme lattice solvent, and the $Li(dme)_3^+$ cation are omitted for clarity.

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 five-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 six-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**.

The extent to which the reactions of **1** with 2.1 equiv of $LiCH_2CMe_3$ (in benzene) or 3.3 equiv of MeLi (in THF) lie toward the side of the products (**2** or **4** and $LiCH_2SiMe_3$) is remarkable and likely[25] reflects the increased basicity of neopentyl and methyl anions in comparison with the (trimethylsilyl)methyl anion,[24] leading to stronger uranium−alkyl bonds. The requirement for addition of more than 2 equiv of $LiCH_2CMe_3$ 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 centers include (1) synthesis of $[\{o\text{-}C_6H_4(N\text{-}Dipp)(PPh(C_6H_4)(=N\text{-}Mes))\}LuMe(THF)_2]$ by treatment of $[\{o\text{-}C_6H_4(N\text{-}Dipp)(PPh(C_6H_4)(=N\text{-}Mes))\}Lu(CH_2SiMe_3)(THF)]$ with 10 equiv of $AlMe_3$ in THF,[26] (2) reaction of $[Me_2Si(2\text{-}Me\text{-}C_9H_5)_2]YMe(THF)]$ with $AlEt_3$ followed by addition of THF to yield an approximately 1:1 mixture of the starting methyl complex and $[Me_2Si(2\text{-}Me\text{-}C_9H_5)_2]YEt(THF)]$,[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,[28−31] trialkylboron,[32] dialkylzinc[30,31,33] or dialkylmagnesium[34] reagent. This last 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 alkyllithium reactions are more scarce but have been reported for dialkylmercury compounds in combination with alkyllithium reagents; these reactions proceed to completion when the alkyllithium product is insoluble in the solvent employed.[36]

The alkyl exchange reactions in this work also bear resemblance to salt metathesis-like reactions 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 = $N(SiMe_3)_2$, $OC_6H_2(CMe_3)_2$-2,6-Me-4; M = Li, X = $CH(SiMe_3)_2$, $^i$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 $[\{CpMn(\mu\text{-}C_2Ph)(THF)\}_2]$,[38] reaction of $[MnCp_2]$ with 1 or 3 equiv of Li(hpp) to afford 0.5 $[\{CpMn(hpp)\}_2]$ or $[\{LiMn(hpp)_3\}_2]$,[39] reaction of $[VCp_2]$ with 2 equiv of Li(hpp) to give 0.25 $[\{V_2(hpp)_4\}Li(\mu\text{-}Cp)Li(\mu\text{-}Cp)Li\{V_2(hpp)_4\}]$-$[CpLi(\mu\text{-}Cp)LiCp]$,[40] and reaction of $[CrCp_2]$ with 2 equiv of Li(MeNCHNMe) to yield 0.5 $[Cr_2(MeNCHNMe)_4]$.[41]

## SUMMARY AND CONCLUSIONS

The preparation and crystallographic characterization of $[(XA_2)U(CH_2SiMe_3)_2]$ (**1**), $[(XA_2)U(CH_2CMe_3)_2]$ (**2**), and $[(XA_2)UMe_3]^-$ (**4**) and in situ syntheses of $[(XA_2)U$-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$(CH_2SiMe_3)_3]^-$ (**3**), $[(XA_2)Th(CH_2CMe_3)_2]$ (**2-Th**), and $[(XA_2)Th(CH_2SiMe_3)(CH_2CMe_3)]$ (**5-Th**) are reported. Reaction of **1** with 2.1 equiv of $LiCH_2CMe_3$ in benzene resulted in rapid conversion to **2** and 2 equiv of $LiCH_2SiMe_3$. 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 equiv of $LiCH_2CMe_3$ proceeds quantitatively to the dineopentyl complex, the analogous reaction of $[(XA_2)Th(CH_2SiMe_3)_2]$ (**1-Th**) requires a significant excess of $LiCH_2CMe_3$ 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. $LiCH_2SiMe_3$ (1.0 M in *n*-pentane) and MeLi (1.60 M in $OEt_2$) solutions were purchased from Sigma-Aldrich, and prior to use, solid $LiCH_2SiMe_3$ 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] $[(XA_2)Th(CH_2SiMe_3)_2]$ (**1-Th**),[3] and $LiCH_2CMe_3$[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 (3.0−0.7 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 (approximately every 30 min) 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 at 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 and 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 protio 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 on the basis of 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 time scale. Furthermore, the para Ar signal always appeared as a triplet at room temperature, allowing definite assignment. The broad signals integrating to 2H and located between −25 and −100 ppm 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) center.

**$[(XA_2)U(CH_2SiMe_3)_2]$ (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 warmed slowly to room temperature; stirring was continued for a total of 12 h. The orange-red solution was evaporated to dryness in vacuo, and the solid residue was extracted with a minimum amount of 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 a minimum amount of *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, 298 K): $\delta$ 12.30, 7.32 (broad s, 2 × 2H, $CH^{1,8}$ and $CH^{3,6}$), 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, 298 K): $\delta$ 11.41, 8.27 (broad s, 2 × 2H, $CH^{1,8}$ and $CH^{3,6}$), 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, 213 K): $\delta$ 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, $CH^{1,8}$ and $CH^{3,6}$), 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, $CHMe_2$), −29.86, −96.02 (v broad s, 2 × 2H, $CHMe_2$). 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 warmed slowly to room temperature; stirring was continued for a total of 12 h. The deep red solution was evaporated to dryness in vacuo, and the solid residue was extracted with a minimum amount of *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 a minimum amount of 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 equiv of $LiCH_2CMe_3$ (0.0021 g, 0.027 mmol) in $C_6D_6$. After approximately 1 h of sonication, $^1$H NMR indicated complete conversion of **1** to **2** (the reaction was usually complete after 20 min) 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. $^1$H NMR ($C_6D_6$, 500.1 MHz, 298 K): $\delta$ 141.1, −142.1 (extremely broad s, 2 × 2H, $UCH_2$), 20.02, −2.43 (v broad s, 2 × 9H, $CH_2CMe_3$), 17.51, 10.17 (v broad s, 2 × 3H, $CMe_2$), 14.71, 4.05 (s, 2 × 2H, $CH^{1,8}$ and $CH^{3,6}$), 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, $CHMe_2$), −27.15, −49.21 (v broad s, 2 × 2H, $CHMe_2$). $^1$H NMR (toluene-$d_8$, 500.1 MHz, 298 K): $\delta$ 134.5, −138.8 (extremely broad s, 2 × 2H, $UCH_2$), 18.78, −2.77 (v broad s, 2 × 9H, $CH_2CMe_3$), 16.66, 9.80 (v broad s, 2 × 3H, $CMe_2$), 14.26, 4.63 (s, 2 × 2H, $CH^{1,8}$ and $CH^{3,6}$), 5.71 (t, $^3J_{H,H}$ = 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, 223 K): $\delta$ 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, $CH^{1,8}$ and $CH^{3,6}$), 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 $[(XA_2)U(CH_2SiMe_3)_2]$·(*n*-pentane) (**1**·(*n*-pentane); 0.010 g, 0.009 mmol) and 1.3 equiv 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


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mixing, $^1$H NMR revealed new signals corresponding to **3**, with concomitant loss of **1**. $^1$H NMR (THF-$d_8$, 500.1 MHz, 298 K): $\delta$ 314.6, 268.8, −161.0 (extremely broad s, 3 × 2H, UC$H_2$), 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, CH$Me_2$), 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, $^3J_{H,H}$ = 7 Hz, 2H, Aryl-para), −1.49, −28.03 (s, 2 × 2H, CH$^{1,8}$ and CH$^{3,6}$), −1.65, −56.37 (v broad s, 2 × 2H, C$H$Me$_2$), −5.34 (s, 18H, $CMe_3$). $^1$H NMR (THF-$d_8$, 500.1 MHz, 223 K): $\delta$ 451.0, 378.0, −236.9 (extremely broad s, 3 × 2H, UC$H_2$), 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, CH$Me_2$), 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, C$H$Me$_2$), −3.37 (broad s, 2H, Aryl-para), −5.28, −40.72 (broad s, 2 × 2H, CH$^{1,8}$ and CH$^{3,6}$), −8.04 (s, 18H, $CMe_3$).

**[Li(dme)$_3$][(XA$_2$)UMe$_3$] (4).** *Method 1.* A mixture of [(XA$_2$UCl$_3${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 warmed slowly to room temperature; stirring was continued for a total of 12 h. 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 min 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, 298 K): $\delta$ 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$^{1,8}$ and 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 and −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$_3$)$_2$]·0.5O(SiMe$_3$)$_2$ (**1-Th**·0.5O(SiMe$_3$)$_2$) (0.020 g, 0.017 mmol) and 15 equiv of LiCH$_2$CMe$_3$ (0.022 g, 0.26 mmol) were taken up in toluene-$d_8$ to afford a colorless 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): $\delta$ 7.25 (broad s, 6H, Aryl-meta and Aryl-para), 6.76, 6.03 (d, $^4J_{H,H}$ = 2 Hz, 2 × 2H, CH$^{1,8}$ and 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): $\delta$ 7.28 (m, $^3J_{H,H}$ = 7 Hz, 4H, Aryl-meta and Aryl-para), 7.16 (d, $^3J_{H,H}$ = 7 Hz, 2H, Aryl-meta), 6.79, 6.14 (s, 2 × 2H, CH$^{1,8}$ and CH$^{3,6}$), 4.19, 3.20 (broad sept, $^3J_{H,H}$ = 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, $^3J_{H,H}$ = 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): $\delta$ 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 (CH$^{1,8}$ and CH$^{3,6}$), 37.94 (ThCH$_2$CMe$_3$), 35.66 (ThCH$_2$C$Me_3$), 35.24 ($CMe_2$), 35.03 ($CMe_3$), 31.67 (C$Me_3$), 29.0 (CHMe$_2$), 26.25, 25.17 (CH$Me_2$). $^{13}$C{$^1$H} NMR (toluene-$d_8$, 150 MHz, 213 K): $\delta$ 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 × ThCH$_2$CMe$_3$), 135.02 (Aryl-C$_{ipso}$), 129.91 (C$^{10,13}$), 128.18, 125.40 (Aryl-C$_{para}$ and Aryl-C$_{meta}$), 110.33, 109.37 (CH$^{1,8}$ and CH$^{3,6}$), 39.11, 36.37 (2 × ThCH$_2$CMe$_3$), 36.05, 23.96 (2 × C$Me_2$), 35.97, 35.35 (2 × ThCH$_2$C$Me_3$), 35.13 ($CMe_2$), 34.90 ($CMe_3$), 31.43 (C$Me_3$), 29.44, 28.08 (2 × CHMe$_2$), 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$_3$)$_2$]·0.5O(SiMe$_3$)$_2$ (**1-Th**·0.5O(SiMe$_3$)$_2$) (0.020 g, 0.017 mmol) and 2.2 equiv of LiCH$_2$CMe$_3$ (0.0030 g, 0.04 mmol) were taken up in toluene-$d_8$ to afford a colorless 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): $\delta$ 7.29, 7.21 (dd, $^3J_{H,H}$ = 7.7 Hz; $^4J_{H,H}$ = 1.7 Hz, 2 × 2H, Aryl-meta), 7.26 (t, $^3J_{H,H}$ = 7.7 Hz, 2H, Aryl-para), 6.77, 6.04 (d, $^4J_{H,H}$ = 2 Hz, 2 × 2H, CH$^{1,8}$ and CH$^{3,6}$), 3.83, 3.32 (broad sept, $^3J_{H,H}$ = 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, $^3J_{H,H}$ = 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$_2$SiMe$_3$), −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): $\delta$ 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$^{1,8}$ and CH$^{3,6}$), 37.44 (ThCH$_2$CMe$_3$), 35.54 (ThCH$_2$C$Me_3$), 35.26 ($CMe_2$), 35.12 ($CMe_3$), 33.87, 28.33 (2 × C$Me_2$), 31.63 (C$Me_3$), 29.43, 28.47 (2 × CHMe$_2$), 26.92, 25.91, 25.46, 24.77 (4 × CH$Me_2$), 3.48 (ThCH$_2$SiMe$_3$).

## ■ ASSOCIATED CONTENT

### Supporting Information

Figures giving $^1$H NMR spectra of **1** (variable temperature), **3** (variable temperatue), **4**, **1-Th**, **2-Th**, and **5-Th** and CIF files giving crystallographic data for **1**, **2**, and **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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### Notes

The authors declare no competing financial interest.

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