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Homoleptic Uranium(IV) Alkyl Complexes: Synthesis and Characterization

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Abstract: The addition of 4.5 equiv of $\mathrm{LiCH_2SiMe_3}$ to $[\mathrm{Li(THF)}]_2[\mathrm{U(O^tBu)_6}]$, in the presence of LiCl, results in the formation of the homoleptic uranium(IV) alkyl complex $[\mathrm{Li_{14}(O^tBu)_{12}Cl}][\mathrm{U(CH_2SiMe_3)_5}]$ (**1**) in low yield. Complex **1** has been characterized by X-ray crystallography. As a solid, **1** is thermally stable for several days at room temperature. However, **1** rapidly decomposes in $\mathrm{C_6D_6}$, as indicated by ^{1}H and $^7\mathrm{Li}\{^1\mathrm{H}\}$ NMR spectroscopy, owing to the lability of the $[\mathrm{Li_{14}(O^tBu)_{12}Cl}]^+$ cation. To avoid the formation of the $[\mathrm{Li_{14}(O^tBu)_{12}Cl}]^+$ counterion, alkylation of $\mathrm{UCl_4}$ was investigated. Treatment of $\mathrm{UCl_4}$ with 5 equiv of $\mathrm{LiCH_2SiMe_3}$ or $\mathrm{LiCH_2{}^tBu}$ at −25 °C in THF/$\mathrm{Et_2O}$ affords $[\mathrm{Li(DME)_3}][\mathrm{U(CH_2SiMe_3)_5}]$ (**2**) and $[\mathrm{Li(THF)_4}][\mathrm{U(CH_2{}^tBu)_5}]$ (**3**), respectively, in good yields. Similarly, treatment of $\mathrm{UCl_4}$ with 6 equiv of MeLi or $\mathrm{KCH_2C_6H_5}$ generates the U(IV) hexa(alkyl) complexes $[\mathrm{Li(TMEDA)}]_2[\mathrm{UMe_6}]$ (**4**) and $\{[\mathrm{K(THF)}]_3[\mathrm{K(THF)_2}][\mathrm{U(CH_2C_6H_5)_6}]_2\}_x$ (**5**) in 38% and 70% yields, respectively. The structures of **3**−**5** have been confirmed by X-ray crystallography. Complexes **2**, **3**, and **5** are thermally stable solids which can be stored at room temperature for several days, whereas **4** decomposes upon warming above −25 °C. The electronic and magnetic properties of **2**, **3**, and **5** were also investigated by NIR spectroscopy and SQUID magnetometry.

Introduction

The organometallic chemistry of uranium is dominated by the use of cyclopentadienyl as a supporting ligand,[1] and the synthesis, bonding, and reactivity of uranium cyclopentadienyl complexes has been extensively studied.[2−14] In contrast, the non-metallocene organometallic chemistry of uranium is considerably less well developed, despite the fact that the search for thermally stable, homoleptic uranium alkyl complexes has been ongoing for over 60 years.[3,15−21] For instance, in the search for volatile uranium compounds for isotope separation, Gilman and co-workers attempted the syntheses of σ-bonded uranium alkyls during the Manhattan project. However, their efforts were unsuccessful and the compounds were presumed to be too unstable to be isolated.[15,16] Nearly three decades passed before the chemistry of these complexes was revisited by Marks and Seyam.[17] Their treatment of $\mathrm{UCl_4}$ with 4 equiv of LiR (R = Me, $\mathrm{CH_2{}^tBu}$, ^{n}Bu, ^{t}Bu, ^{i}Pr) at low temperatures afforded "$\mathrm{UR_4}$" which rapidly decomposed upon warming.[17,20] Several other groups have also explored the reactivity of $\mathrm{UCl_4}$ with alkyl lithium reagents and have reported the formation of finely divided uranium metal[3,17,22−24] or the formation of a U(III) hydride.[19]

The coordinative unsaturation of the metal center in these complexes was reasoned to be the cause of their thermal instability,[2,18] and recognizing this, Wilkinson and Sigurdson treated $\mathrm{UCl_4}$ with excess alkyl lithium reagents to induce 'ate' formation and, thereby, enhance the kinetic stability of the resulting complexes (eq 1). These reactions afforded isolable, homoleptic alkyl uranates with the formulation $[\mathrm{Li(Solvent)_4}]_2$-$[\mathrm{UR_6}]$ (Solvent = THF, $\mathrm{Et_2O}$; R = Me, $\mathrm{C_6H_5}$, $\mathrm{CH_2SiMe_3}$).[18] In

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addition, alkylation of UCl_4 in the presence of TMEDA was proposed to generate the 12-coordinate U(IV) complexes $[Li(TMEDA)_2]_2[UR_6(TMEDA)_3]$, with TMEDA acting as a bidentate ligand, while addition of excess LiR to the uranium(V) alkoxide $U_2(OEt)_{10}$ in dioxane was reported to afford the uranium(V) octa(alkyl) complexes $[Li(dioxane)]_3[UR_8]$. These molecules were characterized by IR and ^{1}H NMR spectroscopy and were described as thermally unstable and *shock sensitive*. However, their formulation, in the absence of any solid-state structural data, has since been called into question.[2]

$$UCl_4 + 6LiR \xrightarrow[\text{THF or Et}_2\text{O}]{-70\ ^\circ\text{C}} \underset{R\,=\,Me,\ C_6H_5,\ CH_2SiMe_3}{[Li(Solvent)_4]_2[UR_6]} \qquad (1)$$

Only one homoleptic uranium alkyl complex has been unambiguously characterized to date. In 1989, Sattelberger and co-workers synthesized $U[CH(SiMe_3)_2]_3$ through the reaction of $U(O\text{-}2,6\text{-}{}^tBu_2C_6H_3)_3$ with 3 equiv of $LiCH(SiMe_3)_2$.[21] Although not coordinatively saturated, kinetic stabilization is afforded by the bulky alkyl ligands. This thermally stable complex was fully characterized, including analysis by X-ray crystallography, but the chemistry of $U[CH(SiMe_3)_2]_3$ has not been pursued further.

The importance of σ-bonded organometallics in organic synthesis,[25−32] combined with their distinctive structures and reactivity,[33−41] makes uranium alkyls an attractive synthetic target. Theoretical analyses of the $U-C_{alkyl}$ σ-bond suggest that the interaction possesses a "significant covalent character"[42] with important contributions from the 6d, and maybe 5f orbitals.[14,43] The participation of the 6d and 5f orbitals in actinide bonding is still the subject of much debate,[44−50] and the isolation of highly symmetric, homoleptic uranium alkyls would provide an excellent platform for further exploring the nature of the uranium−carbon bond.

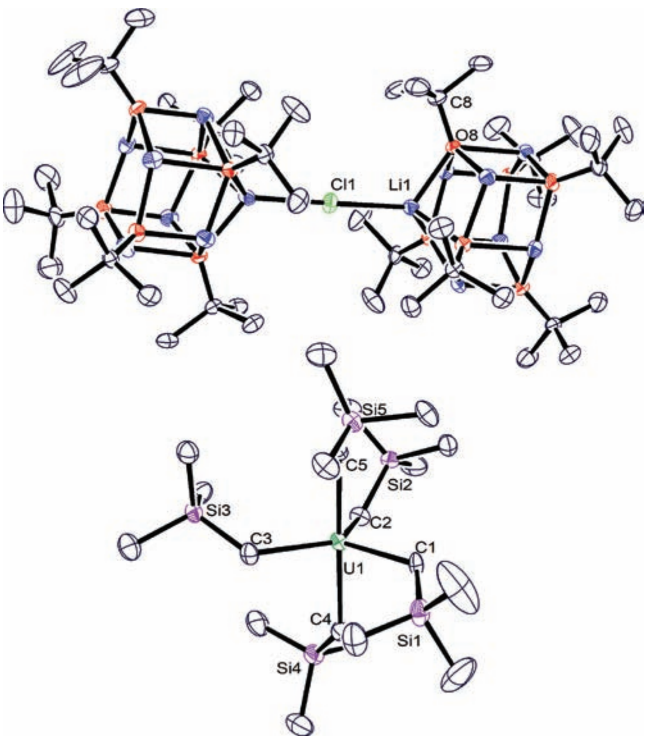

Figure 1. ORTEP diagram of $[Li_{14}(O^tBu)_{12}Cl][U(CH_2SiMe_3)_5]$ (**1**) with 30% probability ellipsoids. Selected bond lengths (Å) and angles (deg): U1−C1 = 2.451(6), U1−C2 = 2.445(6), U1−C3 = 2.461(6), U1−C4 = 2.485(6), U1−C5 = 2.463(5), U1−C1−Si1 = 126.2(3), U1−C2−Si2 = 127.6(3), U1−C3−Si3 = 125.7(3), U1−C4−Si4 = 128.9(3), U1−C5−Si5 = 130.6(3), C1−U1−C2 = 112.8(2), C1−U1−C3 = 122.9(2), C2−U1−C3 = 123.9(2), C1−U1−C4 = 86.9(2), C1−U1−C5 = 92.5(2).

Results and Discussion

Synthesis. We have been exploring the utility of $[Li(THF)]_2[U(O^tBu)_6]$ as a precursor for uranium aryloxide[51] and azido[52] complexes. However, alkyl-for-alkoxide metathesis is also well established, and was employed by Andersen in the synthesis of $UMe_4(dmpe)_2$[53] and by Sattelberger in the synthesis of $U[CH(SiMe_3)_2]_3$.[21] Inspired by these results, we began exploring the reactivity of alkyl lithium reagents with $[Li(THF)]_2[U(O^tBu)_6]$. Thus, addition of excess $LiCH_2SiMe_3$ to $[Li(THF)]_2[U(O^tBu)_6]$ in Et_2O results in immediate formation of a pale green solution. Removal of the solvent in vacuo affords a light green oil. Dissolution in hexanes followed by storage at −25 °C provides bright green crystals, and analysis of this material by X-ray crystallography reveals the formation of an unprecedented homoleptic uranium(IV) alkyl complex $[Li_{14}(O^tBu)_{12}Cl][U(CH_2SiMe_3)_5]$ (**1**).

Complex **1** crystallizes in the orthorhombic space group $P2_12_12_1$, and its solid-state molecular structure is shown in Figure 1. Complex **1** consists of an anionic uranium(IV) center

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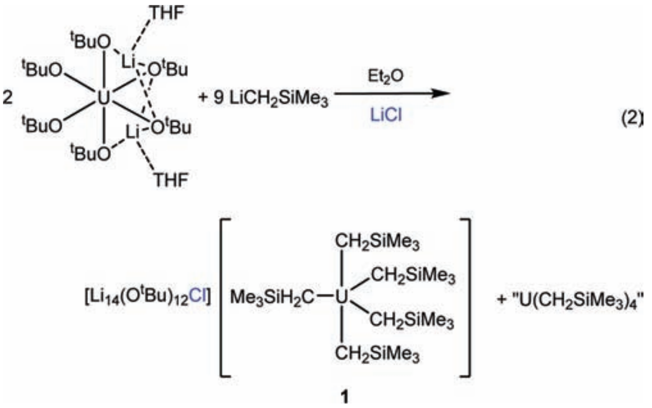
bound by five methyltrimethylsilyl groups in a trigonal bipyramidal arrangement. The U−C bond lengths in **1** range from U1−C2 = 2.445(6) Å to U1−C4 = 2.485(6) Å with U−C−Si bond angles ranging from U1−C3−Si3 = 125.7(3)° to U1−C5−Si5 = 130.6(3)°. Only one other uranium(IV) complex possessing a methyltrimethylsilyl ligand has been structurally characterized, namely $[(2,6\text{-}{}^{i}Pr_2C_6H_3NCH_2CH_2)_2O]U(CH_2SiMe_3)_2$,[54] and its U−C bond distances (U−C = 2.40(2) Å, 2.44(2) Å) and U−C−Si bond angles (U−C−Si = 129.7(10)°, 127.0(11)°) are comparable to those found for **1**. Furthermore, the U−C bond lengths in **1** are within the range of other reported $U(IV)-C_{alkyl}$ distances (ca. 2.4−2.5 Å).[55−66]

The cation in **1**, $[Li_{14}(O^{t}Bu)_{12}Cl]^+$, consists of two heptalithium clusters bridged by a single chloride ion. Each heptamer fragment is formed by capping the well-known $LiO^{t}Bu$ hexamer structure with a single lithium cation,[67] and its metrical parameters are consistent with other structurally characterized lithium *tert*-butoxide clusters.[67,68] The chloride ion found in $[Li_{14}(O^{t}Bu)_{12}Cl]^+$ likely originates from residual LiCl present from the initial synthesis of $[Li(THF)]_2[U(O^{t}Bu)_6]$.[69]

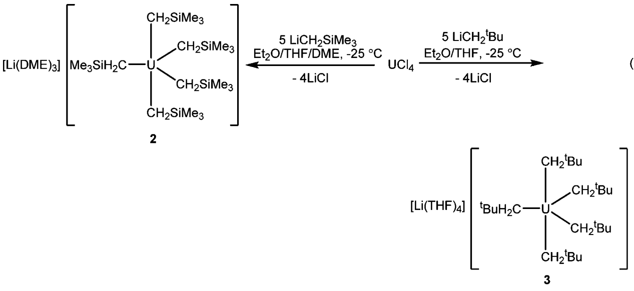
As indicated by its solid-state molecular structure, the formation of **1** requires 14 lithium ions. Since only two lithium ions can come from each uranium complex, and one is associated with the chloride ion, the synthesis of **1** requires at least one sacrificial equivalent of $[Li(THF)]_2[U(O^{t}Bu)_6]$ to generate the cation. Thus it is possible that the tetra(alkyl) complex $U(CH_2SiMe_3)_4$ is also formed (eq 2), but based upon previous observations of uranium(IV) alkyl reactivity,[15−17,20] it is unlikely to be thermally stable and probably decomposes during the course of the reaction.



(2)

A rational synthesis of **1** can be achieved by addition of 4.5 equiv of $LiCH_2SiMe_3$ to an Et_2O solution of $[Li(THF)]_2[U(O^{t}Bu)_6]$ in the presence of excess LiCl (eq 2). By this route, **1** can be isolated in 38% yield as a pale green solid. In the crystalline state, **1** is thermally stable for several days at room temperature and is indefinitely stable at −25 °C. Complex **1** is insoluble in hexanes but completely soluble in benzene or ethereal solvents; however, it appears to be unstable in these solutions at room temperature as it changes from pale green to light brown within minutes. The ^1H NMR spectrum of **1** in C_6D_6, taken immediately upon dissolution of the sample, exhibits two singlets at −13.69 and 18.42, in a 9:2 ratio. These peaks are assignable to the methyl and methylene protons of the methyltrimethylsilyl ligand, respectively. Additionally, two other peaks are observed at 1.12 and 1.22 ppm, which we attribute to the protons of the *tert*-butoxide groups originating from the $[Li_{14}(O^{t}Bu)_{12}Cl]^+$ cation. The resonance at 1.22 ppm is similar to that exhibited by free $LiO^{t}Bu$, suggesting that the cluster breaks apart in solution. The ^1H NMR spectrum of **1** is also complicated by the presence of several additional peaks, whose intensities quickly increase on standing. This complicated solution phase behavior is further reflected by the six resonances exhibited in its $^7Li\{^1H\}$ NMR spectrum.

The thermal stability of crystalline samples of **1** contrasts with that of previously generated homoleptic uranium(IV) alkyl complexes,[15−17,20] and coordination by five methyltrimethylsilyl ligands probably affords the complex some kinetic stabilization. However, $[Li_{14}(O^{t}Bu)_{12}Cl]^+$ is a poor counterion, given its lability in solution, and to avoid its formation we have explored the use of UCl_4 as a starting material. Addition of a THF solution of UCl_4 to a stirring solution of 5 equiv of $LiCH_2SiMe_3$ in Et_2O at −25 °C results in the formation of a deep green solution, concomitant with deposition of a white powder. Filtration of the mixture and removal of the solvent in vacuo afford a bright green solid. Recrystallization of the material from an Et_2O/DME/hexanes mixture provides crystals of $[Li(DME)_3][U(CH_2SiMe_3)_5]$ (**2**) in 82% yield (eq 3). Similar treatment of UCl_4 with 5 equiv of $LiCH_2{}^{t}Bu$ affords the orange neopentyl analogue, $[Li(THF)_4][U(CH_2{}^{t}Bu)_5]$, in 73% yield (eq 3).



(3)

Single crystals of **2** suitable for X-ray crystallographic analysis have not been forthcoming. However, X-ray quality

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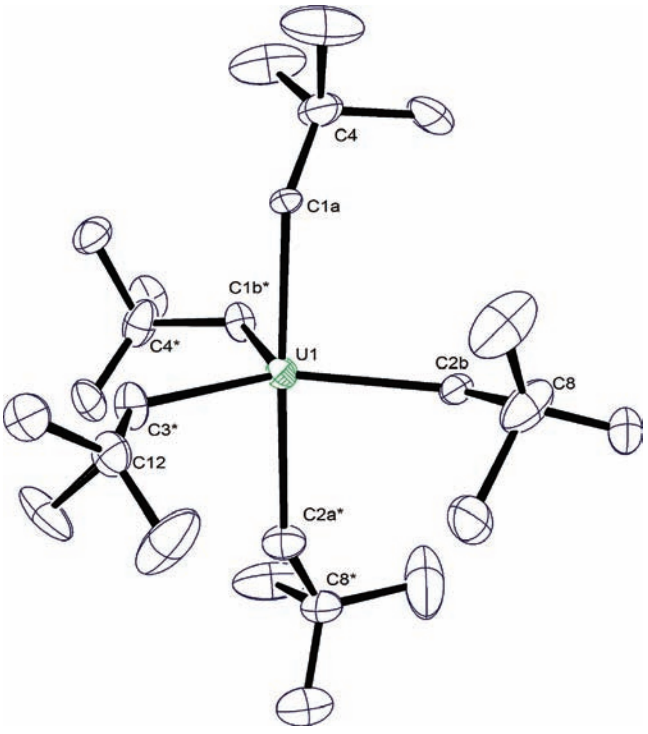


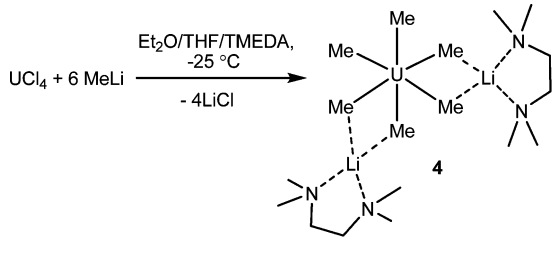
Figure 2. ORTEP diagram of one orientation of $[Li(THF)_4][U(CH_2{}^tBu)_5]$ (**3**) with 30% probability ellipsoids. $[Li(THF)_4]^+$ fragment not shown. Selected bond lengths (Å) and angles (deg): U−C1a = 2.47(1), U−C1b* = 2.49(1), U−C2a* = 2.51(1), U−C2b = 2.47(2), U−C3* = 2.51(1), U−C1a−C4 = 139(1), U1−C1b*−C4* = 126.3(7), U1−2a*−C8* = 149(1), U1−2b−C8 = 136(1), U1−C3*−C12 = 132.7(8), C1a−U1−C1b* = 90.1(5), C1b*−U1−C2b = 116.6(5), C1b*−U1−C3* = 111.3(4), C2b−U1−C3* = 132.1(5), C1b*−U1−C2a* = 91.3(4).

crystals of **3** can be grown from a hexanes/Et_2O solution. Complex **3** crystallizes in the monoclinic space group $P2_1/m$ and consists of discrete cation/anion pairs. The anion in **3** consists of a uranium ion ligated by five neopentyl ligands. In the solid state, each neopentyl ligand is disordered over two positions. In addition, U1 lies on a special position, and two of the five neopentyl ligands are generated by symmetry. As a result, the complex can be described as trigonal bipyramid disordered over two orientations, with one orientation shown in Figure 2. The U−C distances of **3** (av. U−C = 2.49(3) Å) are comparable to those observed for **1** and other U(IV)−C_{alkyl} complexes. The U−C−C bond angles in **3** range from U1−C1b*−C4* = 126.3(7)° to U1−C2a*−C8* = 149(1)°. However, this latter U−C−C angle is much larger than expected and may be an artifact of the neopentyl disorder. To our knowledge, **3** is the first structurally characterized neopentyl-containing uranium complex. Complex **3** also contains a lithium cation bound by four THF molecules in a tetrahedral arrangement. The metrical parameters of the $[Li(THF)_4]^+$ cation are similar to those previously observed for this moiety.[70]

The ^1H NMR spectrum of **2** in a 5:1 C_6D_6/THF-d_8 solution consists of two singlets in a 9:2 ratio at −2.15 and 17.80 ppm, respectively. We have assigned these peaks to the methyl and methylene protons, respectively. The ^1H NMR spectrum of **3** in THF-d_8 displays two resonances at 2.77 and 26.44 ppm (in a 9:2 ratio, respectively), also assignable to methyl and methylene protons. The $^7Li\{^1H\}$ NMR spectra of **2** and **3** each consist of singlets at −4.96 and 0.15 ppm, respectively. Cooling THF-d_8 solutions of **2** or **3** does not result in decoalescence of the methyl or methylene resonances, and only one set of alkyl groups is observed at −90 °C. A plot of δ versus $1/T$ for the methyl and methylene protons is consistent with Curie Law behavior (see Supporting Information).

Complexes **2** and **3** are thermally stable solids which can be stored at room temperature, under an inert atmosphere, for several days without decomposition. These materials can also be stored indefinitely at −25 °C. In our hands, neither material appears to be shock sensitive. Both **2** and **3** are insoluble in nonpolar solvents such as hexanes but are very soluble in ethereal solvents. Unlike complex **1**, complexes **2** and **3** appear to be stable in solutions of THF at room temperature for several hours, but after 24 h, both complexes begin to decompose, with **3** decomposing at a faster rate. These observations are consistent with the greater stability typically afforded to methyltrimethylsilyl complexes in comparison to neopentyl complexes.[18,71,72] Both **2** and **3** are unstable in aromatic solvents. Complex **2** slowly decomposes in the presence of C_6D_6, over the course of 24 h, affording $SiMe_4$ as the only observable product in the ^1H NMR spectrum. Dissolution of **3** in C_6D_6 results in an immediate color change, affording an intractable black solution. These samples contain neopentane as the only observable product in the ^1H NMR spectrum. Interestingly, the slow decomposition of $U[CH(SiMe_3)_2]_3$ in C_6D_6 was also observed.[21] The activation of aryl C−H bonds by uranium(IV) alkyl complexes has been previously observed, yielding U−C_{aryl} products,[73,74] and we are currently endeavoring to characterize the uranium-containing materials generated from these reactions. Additionally, we have found that **2** and **3** are exceedingly sensitive to the impurities present in commercially available THF-d_8, and the dissolution of either **2** or **3** in THF-d_8 often results in partial decomposition. As such, we have found that nondeuterated solvents, such as protio THF and DME, are useful for the NMR characterization of these alkyl complexes. The ^1H resonances of **2** and **3** are not obscured by the solvent resonances owing to their paramagnetism. Finally, treatment of 6 equiv of $LiCH_2SiMe_3$ with UCl_4 does not generate $[Li(Solvent)_4][U(CH_2SiMe_3)_6]$ as reported by Wilkinson[18] but instead affords **2** as the only observed product. Similarly, addition of UCl_4 to 6 equiv of $LiCH_2{}^tBu$ generates only complex **3**.

We have also explored the synthesis of a homoleptic uranium methyl complex. Addition of a THF solution of UCl_4 to 6 equiv of MeLi in Et_2O/TMEDA at −25 °C results in the formation of a deep orange solution concomitant with precipitation of a white powder. Filtration of this mixture and removal of the solvent in vacuo affords an orange solid. Recrystallization from Et_2O/hexanes provides crystals of $[Li(TMEDA)]_2[UMe_6]$ (**4**) in 38% yield (eq 4). During the synthesis and workup, solutions of **4** must be maintained at low temperatures, as it quickly decomposes on warming above −25 °C.



4

(4)

Complex **4** crystallizes in the orthorhombic space group *Pbca*, and its solid state molecular structure is shown in Figure 3.

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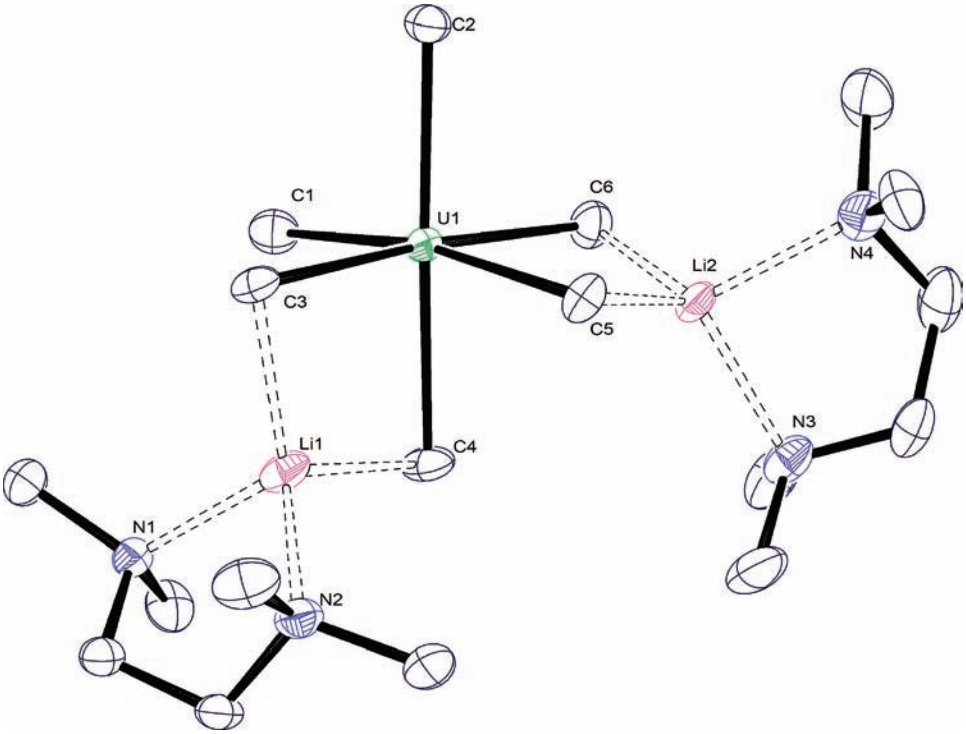

Figure 3. ORTEP diagram of $[Li(TMEDA)]_2[UMe_6]$ (**4**) with 30% probability. Selected bond lengths (Å) and angles (deg): U1−C1 = 2.48(1), U1−C2 = 2.483(9), U1−C3 = 2.564(9), U1−C4 = 2.557(9), U1−C5 = 2.600(9), U1−C6 = 2.55(1), Li1−C3 = 2.21(2), Li1−C4 = 2.19(2), Li2−C5 = 2.18(2), Li2−C6 = 2.26(2), C1−U1−C2 = 94.8(3), C1−U1−C3 = 89.4(3), C1−U1−C4 = 85.9(3), C1−U1−C5 = 170.1(3), C1−U1−C6 = 96.4(3), C2−U1−C5 = 93.8(3).

Complex **4** exhibits an octahedral coordination geometry in the solid state, and its two lithium cations are contained within the secondary coordination sphere. Each lithium ion is ligated by two methyl groups and one TMEDA molecule, affording it an overall tetrahedral geometry. The terminal U−C distances (U1−C1 = 2.48(1) Å, U1−C2 = 2.483(9) Å) in **4** are comparable to other reported $U-C_{methyl}$ distances.[56−62,64] In addition, coordination of the lithium cation to the methyl group results in a lengthening of the bridging U−C bonds (U1−C3 = 2.564(9) Å, U1−C4 = 2.557(9) Å, U1−C5 = 2.600(9) Å, and U1−C6 = 2.55(1) Å). The Li−C distances (av. 2.21(4) Å) are comparable to those observed in similar methyl-bridged complexes.[75,76]

Complex **4** is similar to $[Li(TMEDA)]_3[LnMe_6]$ (Ln = Ho,[76] Er,[77] Lu[78]) and $[Li(TMEDA)]_3[ThMe_7]$,[75] which have all been structurally characterized. However, these complexes are thermally stable, decomposing well above room temperature.[76] Notably, in our system, addition of UCl_4 to 7 equiv of MeLi leads to the formation of complex **4** as the only isolated product, consistent with the smaller ionic radius of U^{4+} versus Th^{4+}.[79] The structure of $[Li(TMEDA)]_2[ZrMe_6]$ has also been determined.[80] The trigonal prismatic geometry of this complex is explained by invoking the participation of Zr 4*d* orbitals in the M−C *σ* bonds. As such, the octahedral structure of **4** suggests that the U 6*d* orbitals are not significantly involved in metal−ligand bonding.

The ^1H NMR spectrum of **4** in THF-d_8 at −25 °C consists of a single broad resonance at −19.92 ppm assignable to the methyl protons. The presence of a single peak suggests that lithium cations are completely solvated by THF or are rapidly exchanging between the available binding sites around the $[UMe_6]^{2-}$ ion. Additionally, the TMEDA resonances appear as two broad overlapping singlets at 2.25 and 2.30 ppm. The $^7Li\{^1H\}$ NMR spectrum of **4** displays a single broad resonance at 7.72 ppm.

The synthesis of **4** in the absence of TMEDA, using only THF or DME as the solvent, results in a light orange product that quickly decomposes to an intractable brown solid within a few hours, even when stored at −25 °C. This is consistent with the observations of Wilkinson and Sigurdson, who also found that the TMEDA adducts were much more stable than the Et_2O and THF adducts.[18] Interestingly, the hexamethyl complexes synthesized by Wilkinson and Sigurdson, including $[Li(TMEDA)_2]_2[UR_6(TMEDA)_3]$, were described as being olive to dark green materials. In our hands, **4** is a light orange solid which turns brown upon decomposition.

We have also pursued the synthesis of a uranium(IV) benzyl complex. Thus, treatment of UCl_4 with 6 equiv of $KCH_2C_6H_5$ in THF results in the formation of a dark red solution. Filtration of the reaction mixture and recrystallization from THF/hexanes

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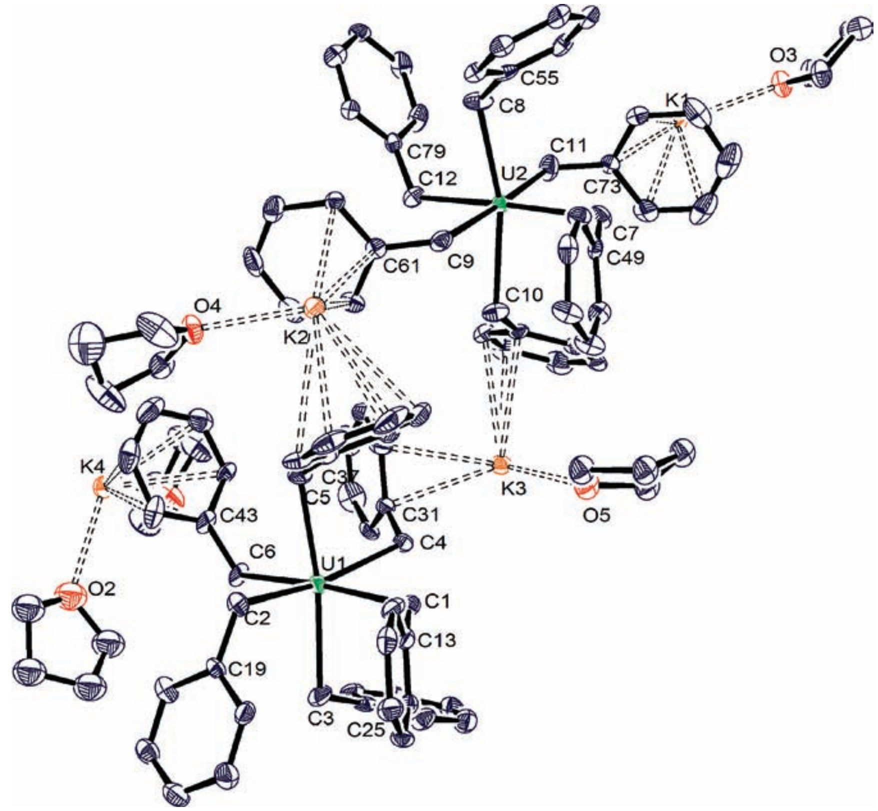
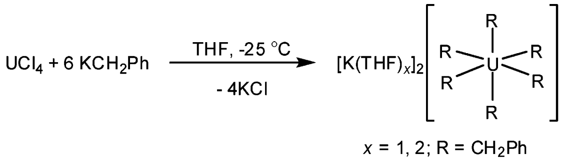


Figure 4. ORTEP diagram of the asymmetric unit in crystals of $\{[K(THF)]_3[K(THF)]_2[U(CH_2C_6H_5)_6]_2\}_x$ (**5**) with 30% probability ellipsoids. Selected bond lengths (Å) and angles (deg): U2−C7 = 2.53(2), U2−C8 = 2.50(2), U2−C9 = 2.56(2), U2−C10 = 2.54(2), U2−C11 = 2.57(2), U2−C12 = 2.53(2), K1−C73 = 3.17(2), K1−C74 = 3.27(2), K1−C77 = 3.23(2), K1−C78 = 3.12(2), K2−C61 = 3.16(2), K2−C62 = 3.28(2), K2−C65 = 3.35(2), K2−C66 = 3.17(2), U2−C7−C49 = 111(1), U2−C8−C55 = 124(1), U2−C9−C61 = 117(1), U2−C10−C67 = 121(1), U2−C11−C73 = 109(1), U2−C12−C79 = 122(1), C7−U2−C8 = 97.6(7), C8−U2−C9 = 85.7(6), C8−U2−C10 = 164.6(7), C8−U2−C11 = 93.7(7), C8−U2−C12 = 89.1(6).

afford $\{[K(THF)]_3[K(THF)_2][U(CH_2C_6H_5)_6]_2\}_x$ (**5**) as a dark red crystalline material in 70% yield (eq 5).



(5)

5

Complex **5** crystallizes in the monoclinic space group $P2_1/c$. The asymmetric unit of **5** contains two crystallographically independent uranium centers, each ligated by six benzyl groups (Figure 4). The asymmetric unit also contains four crystallographically independent potassium cations. Each potassium ion participates in π-interactions with up to three benzyl rings, resulting in the formation of an extended 3D solid. The potassium ions exhibit μ-η^6:η^6, μ_3-η^2:η^3:η^6, or μ_3-η^4:η^4:η^6 coordination modes with the phenyl rings. Similar π-interactions have been observed in other systems.[81,82] The potassium ions in **5** are also coordinated by either one or two THF molecules.

The metrical parameters of the two independent uranium complexes in **5** are similar, and only one will be discussed in detail. The uranium center in **5** exhibits a distorted octahedral geometry (e.g., C7−U2−C8 = 97.6(7)°, C8−U2−C9 = 85.7(6)°, and C8−U2−C10 = 164.6(7)°). The U−C$_{benzyl}$ bond lengths of **5** (U2−C7 = 2.53(2) Å, U2−C8 = 2.50(2) Å, U2−C9 = 2.56(2) Å, U2−C10 = 2.54(2) Å, U2−C11 = 2.57(2) Å, U2−C12 = 2.53(2) Å) are comparable to other known U(IV)−C$_{benzyl}$ distances.[57,60,61,63,65] As indicated by the U−C−C bond angles (U2−C7−C49 = 111(1)°, U2−C8−C55 = 124(1)°, U2−C9−C61 = 117(1)°), each of the benzyl ligands is η^1.

As a crystalline solid, **5** can be stored at room temperature, under inert atmosphere, for up to one day, and it can be stored indefinitely at −25 °C. Complex **5** is insoluble in nonpolar solvents such as hexanes or toluene but quite soluble in THF. Its ^{1}H NMR spectrum in a 1:5 C_6D_6/THF-h_8 solution consists of a broad resonance at −25.88 ppm, corresponding to the methylene protons of the benzyl ligand, and two broad resonances at 2.87 and 7.36 ppm, assignable to the aryl protons. These resonances are observed in a 2:3:2 ratio, respectively. The K$^+$−arene interactions are not likely maintained in solution, as only one set of signals is observed for the benzyl group. Interestingly, treatment of UCl_4 with $Mg(CH_2C_6H_5)_2$ is also reported to yield an 'ate' complex, formulated as $U(CH_2C_6H_5)_4 \cdot MgCl_2$.[83] A homoleptic benzyl complex of thorium(IV) is also known, namely $Th(CH_2C_6H_5)_4$,[84] but to our knowledge it has not been structurally characterized.

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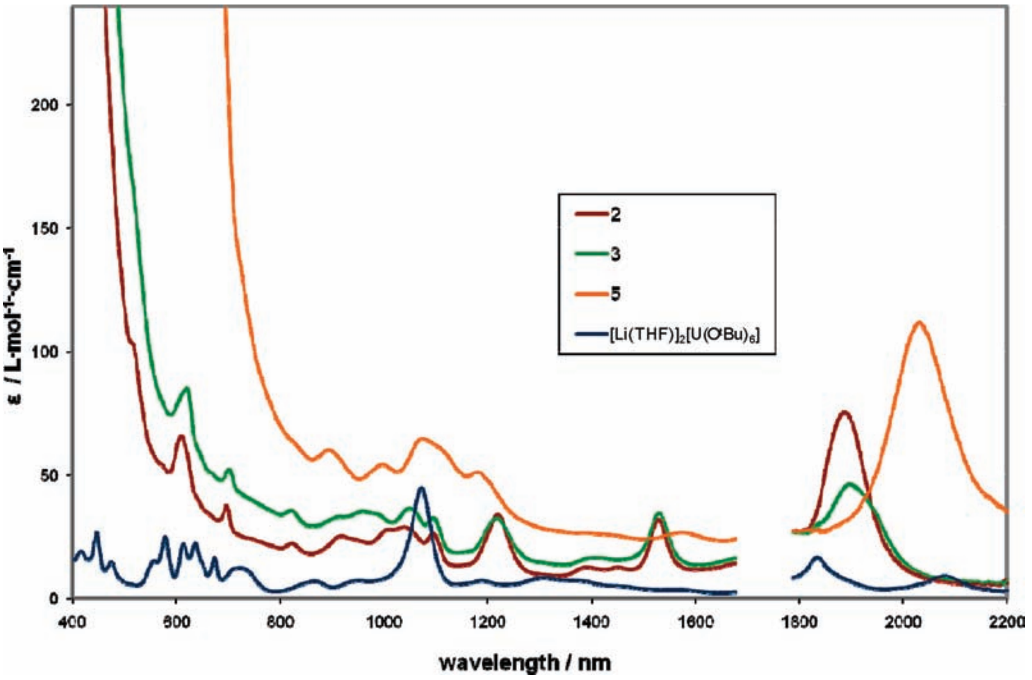

Figure 5. Room temperature NIR absorption spectra for **2** (3.20 mM, THF), **3** (5.22 mM, THF), **5** (3.30 mM, THF), and $[Li(THF)]_2[U(O^tBu)_6]$ (9.51 mM, THF).

A comparison of the solid state molecular structures of complexes **1** and **3**−**5** with $[Li(THF)]_2[U(O^tBu)_6]$ may allow us to draw inferences regarding the π-accepting ability of uranium. The U−O−C$_\alpha$ angle of uranium alkoxides has been used as evidence for U−O π-interactions.[51,69,85−88] However, the large M−O−C angle can also be solely interpreted as an electrostatic effect.[89] Based upon the analysis made by Rothwell and co-workers,[90] an M−C$_{alkyl}$ bond should be 0.10−0.15 Å longer than a purely σ-bonded M−O$_{alkoxide}$ interaction. $[Li(THF)]_2[U(O^tBu)_6]$ exhibits U−O bond distances of 2.137(9) and 2.140(8) Å for its terminal alkoxide bonds,[69] whereas complexes **1** and **3**−**5** exhibit average U−C distances of 2.46(1), 2.49(3), 2.48(1), and 2.55(6) Å, respectively, for their terminal alkyl ligands. These bonds are 0.31−0.41 Å longer than the U−O bonds of $[Li(THF)]_2[U(O^tBu)_6]$, significantly longer than the 0.10−0.15 Å anticipated for a purely σ-interaction, and suggests that π-bonding plays a large role in the overall bonding interaction of U(IV) alkoxides.

UCl_4 has been described as a troublesome starting material for the synthesis of homoleptic uranium(IV) alkyl complexes.[3,19−21,75] For instance, Seyam and co-workers noted that the reactivity of alkylating reagents toward UCl_4 is highly batch dependent and sensitive to the method of stirring.[20] In their experiments, thionyl chloride was often used to dry the UCl_4. This latter step may have been detrimental if some $SOCl_2$ remained trapped in the solid. In contrast, we prepare our UCl_4 from UO_3 using the standard literature procedure[66,91] and rinse the resulting solid with copious amounts of CH_2Cl_2 and hexanes. Using these conditions we have found that our alkylation reactions are reproducible from batch to batch. Another reason for our success is likely our addition of UCl_4, as a THF solution, to a solution of the alkylating reagent, as this results in the rapid steric saturation of the U(IV) metal center and minimizes the formation of the thermally unstable tetra(alkyl) complexes. Notably, reduction of U(IV) is not observed under these conditions.

Electronic Absorption Spectroscopy. The NIR absorption spectra, recorded in THF, for complexes **2**, **3**, **5**, and $[Li(THF)]_2[U(O^tBu)_6]$ are shown in Figure 5. The bands observed in this region represent the formally Laporte forbidden f→f transitions of the U^{4+} $5f^2$ ion.[92,93] As illustrated in Figure 5, $[Li(THF)]_2[U(O^tBu)_6]$ exhibits the lowest molar absorptivity values ($\varepsilon = 3-45$ L·mol^{-1}·cm^{-1}). $[Li(THF)]_2[U(O^tBu)_6]$ possesses a pseudo-octahedral geometry which, as a result of the high symmetry, may decrease the intensity of the f→f transitions. Complexes **2**, **3**, and **5** exhibit molar absorptivities slightly greater than those displayed by $[Li(THF)_2][U(O^tBu)_6]$, with values comparable to those observed for U(IV) alkyl metallocene complexes.[93] Complexes **2** and **3** exhibit nearly identical NIR absorption spectra, confirming their structural similarity. Based on symmetry, complex **5** should exhibit absorption values close to those displayed by $[Li(THF)_2][U(O^tBu)_6]$. However, the molar absorptivities of **5** are considerably greater ($\varepsilon = 26-260$ L·mol^{-1}·cm^{-1}). The reason for this disparity is not known.

Magnetic Susceptibility. To gain further insight into the electronic properties of our uranium alkyl complexes, we determined the magnetic susceptibility of **2**, **3**, **5**, and

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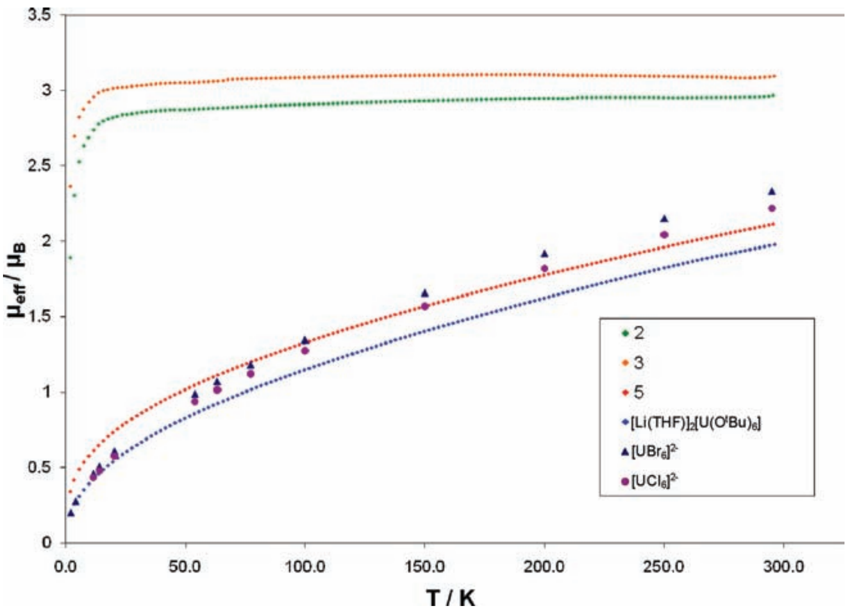

Figure 6. Temperature dependence of effective magnetic moment for **2**, **3**, **5**, $[Li(THF)]_2[U(O^tBu)_6]$, $[Ph_3BuP]_2[UCl_6]$, and $[Ph_3BuP]_2[UBr_6]$. Data for $[Ph_3BuP]_2[UCl_6]$ and $[Ph_3BuP]_2[UBr_6]$ calculated from ref 94.

$[Li(THF)]_2[U(O^tBu)_6]$ using SQUID magnetometry. In particular, the presence of strong field ligands, such as $Me_3SiCH_2^-$ and $^tBuCH_2^-$, raises the possibility that crystal field splitting, and not spin–orbital coupling, will dominate the magnetic behavior of these complexes. A plot of effective magnetic moments versus temperature is shown in Figure 6. At 295 K, complexes **2**, **3**, **5**, and $[Li(THF)]_2[U(O^tBu)_6]$ exhibit effective magnetic moments of 2.96, 3.09, 2.11, and 1.98 μ_B, respectively. These values are significantly smaller than the 3.58 μ_B calculated for the free $5f^2$ ion in a $^3H_4$ ground state.[92,95] Reduced effective magnetic moments, versus that of the free ion value, have been attributed to quenching of the spin–orbit coupling via covalent metal–ligand interactions.[63,92,95–99] Moreover, a comparison of the effective magnetic moments of **5** and $[Li(THF)]_2[U(O^tBu)_6]$ with the literature values reported for $[Ph_3BuP]_2[UCl_6]$ (2.22 μ_B at 295 K) and $[Ph_3BuP]_2[UBr_6]$ (2.33 μ_B at 295 K) reveals a clear correlation with ligand field strength.[94] Thus, the low effective magnetic moments of **5** and $[Li(THF)]_2[U(O^tBu)_6]$, relative to $[UCl_6]^{2-}$ and $[UBr_6]^{2-}$, can be attributed to the presence of stronger field ligands around the U^{4+} ion. The slightly lower effective magnetic moment of $[Li(THF)]_2[U(O^tBu)_6]$ versus **5** may be due to the butoxide ligand's ability to use its lone pairs in bonding with uranium,[51,69] which further quenches the spin–orbit coupling. The temperature dependence of the effective magnetic moments in **5** and $[Li(THF)]_2[U(O^tBu)_6]$ and their low magnetic moments at 2 K (0.34 and 0.20 μ_B, respectively) are in line with other U(IV) complexes.[63,95,97–100] This behavior is usually attributed to the presence of a singlet ground state combined with the effects of temperature-independent paramagnetism.[97,101]

Surprisingly, complexes **2** and **3** exhibit the highest effective magnetic moments at room temperature. In addition, **2** and **3** possess larger magnetic moments at 2 K (1.89 and 2.36 μ_B, respectively) in comparison to most U(IV) complexes.[97] The difference in magnetic behavior could be attributed to the trigonal bypramidal geometry of complexes **2** and **3**, which leads to a change in the crystal field splitting pattern and results in a different ground state than the octahedral case. In D_{3h} symmetry, the f orbitals are split into a_2', a_1'', a_2'', e', and e'' components.[102] Thus, in **2** and **3** the e'' set could be occupied in the ground state, resulting in a significantly different magnetic response than that observed for complexes in an O_h geometry. Support for this comes from the spectroscopic analysis of $Nd(N\{SiMe_3\}_2)_3(CNCy)_2$, which suggests that the degenerate f_{xyz} and $f_{z(x^2-y^2)}$ orbitals (the e'' set) are the lowest energy f orbitals.[103] A similar rationale has been invoked to explain the magnetic behavior of $UBr_4(Et_3AsO)_2$, which exhibits a large tetragonal distortion and possibly an e ground state.[101,104] Comparable low-temperature behavior with **2** and **3** has also been observed in another U(IV) complex, namely $((^{tBu}ArO)_3tacn)U(OC^{tBu}Ph_2)$;[100] however this complex possesses a ligand-centered radical, in addition to the paramagnetic U(IV) center. It should be noted, however, that this qualitative model is probably one of many that could describe the magnetic behavior of these alkyl complexes, and as such further experimental and theoretical studies will be required to fully understand the origins of their magnetic properties.

Summary

Treatment of UCl_4 with various alkylating reagents affords the homoleptic alkyl complexes $[Li(DME)_3][U(CH_2SiMe_3)_5]$,

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$[Li(THF)_4][U(CH_2{}^tBu)_5]$, $[Li(TMEDA)]_2[UMe_6]$, and $\{[K(THF)]_3[K(THF)_2][U(CH_2C_6H_5)_6]_2\}_x$ in good yields. The thermal stability of these complexes, with the exception of $[Li(TMEDA)]_2[UMe_6]$, is likely imparted by the steric saturation of the uranium metal center via 'ate' formation and greatly contrasts with the noted instability of "UR_4".[2,3,15−17,19,20] Additionally, $[Li(DME)_3][U(CH_2SiMe_3)_5]$, $[Li(THF)_4][U(CH_2{}^tBu)_5]$, and $\{[K(THF)]_3[K(THF)_2][U(CH_2C_6H_5)_6]_2\}_x$ have been characterized by NIR spectroscopy and SQUID magnetometry. Comparison of their spectroscopic and magnetic properties with other homoleptic uranium(IV) systems, such as $[Li(THF)]_2[U(O^tBu)_6]$, reveals that their electronic structures are highly influenced by the nature and number of ligands coordinated to the metal in a manner that is reminiscent of the transition metals. We will continue to investigate the coordination chemistry of these homoleptic uranium(IV) alkyls to better understand the bonding and reactivity of the uranium−carbon interaction in these high symmetry complexes.

Experimental Section

General. All reactions and subsequent manipulations were performed under anaerobic and anhydrous conditions under either high vacuum or an atmosphere of argon or nitrogen. Diethyl ether, hexanes, and THF were dried using a Vacuum Atmospheres DRI-SOLV Solvent Purification system. DME was distilled from sodium benzophenone ketyl. TMEDA was stored over activated 4 Å molecular sieves for 24 h prior to use. All deuterated solvents were purchased from Cambridge Isotope Laboratories Inc. and were dried over activated 4 Å molecular sieves for 24 h prior to use. $[Li(THF)]_2[U(O^tBu)_6]$,[69] UCl_4,[66] $LiCH_2{}^tBu$,[105] and $KCH_2C_6H_5$[106] were synthesized according to the published procedures. All other reagents were obtained from commercial sources and used as received.

NMR spectra were recorded on a Varian UNITY INOVA 400 or a Varian UNITY INOVA 500 spectrometer. ^1H NMR spectra are referenced to external $SiMe_4$ using the residual protio solvent peaks as an internal standard. $^7Li\{^1H\}$ NMR spectra are referenced to an external saturated solution of LiCl in deuterium oxide. UV−vis/NIR spectra were recorded on a UV-3600 Shimadzu spectrophotometer. Elemental analyses were performed by the Micro-Mass Facility at the University of California, Berkeley.

Magnetism Measurements. Magnetism data were recorded using a Quantum Design MPMS 5XL SQUID magnetometer. All experiments were performed using a 1 T field between 2 and 295 K. Crystalline, powdered samples containing ca. 50−100 mg of compound were loaded, under an inert atmosphere, into a Teflon-lined gelatin capsule and packed with approximately 20 mg of quartz wool. The sample was positioned within a plastic straw for analysis. The data were not corrected for the contribution of the gelatin capsule/straw sample holder. Diamagnetic corrections ($\chi_{dia} = 5.70 \times 10^{-4}$ $cm^3 \cdot mol^{-1}$ for **2**, 5.55×10^{-4} $cm^3 \cdot mol^{-1}$ for **3**, 5.85×10^{-4} $cm^3 \cdot mol^{-1}$ for **5**, and 4.71×10^{-4} $cm^3 \cdot mol^{-1}$ for $[Li(THF)]_2[U(O^tBu)_6]$) were made using Pascal's constants.[107]

$[Li_{14}(O^tBu)_{12}Cl][U(CH_2SiMe_3)_5]$ (1). To a stirring mixture of $[Li(THF)]_2[U(O^tBu)_6]$ (0.077 g, 0.092 mmol) and LiCl (0.006 g, 0.142 mmol) in Et_2O (2 mL) was added a solution of $LiCH_2SiMe_3$ (0.415 mL, 0.415 mmol, 1.0 M in pentane) dropwise. The resulting pale green solution was stirred for 5 min, and the solvent was removed in vacuo affording a bright green oil. The oil was dissolved in hexanes (2 mL), and the solution was filtered through a Celite column (2 cm × 0.5 cm) supported on glass wool. The volume of the filtrate was reduced in vacuo, and the solution cooled to −25 °C for 24 h, resulting in the deposition of bright green crystals. The solid was washed with hexanes (2 × 2 mL) and dried under vacuum. 0.029 g, 38% yield. ^1H NMR (500 MHz, 22 °C, C_6D_6): δ −13.69 (s, 45H, $CH_2Si\mathit{Me_3}$), 1.12 (s, 72H, CCH_3), 1.22 (s, 36H, CCH_3), 18.42 (br s, 10H, $\mathit{CH_2}SiMe_3$). $^7Li\{^1H\}$ NMR (194 MHz, 22 °C, C_6D_6): δ −3.88 (s), −2.85 (s), −1.84 (s), −1.63 (s), −1.30 (s), −0.99 (s). Anal. Calcd for $C_{68}H_{163}ClLi_{14}O_{12}Si_5U$: C, 48.49; H, 9.77. Found: C, 48.70; H, 9.91.

$[Li(DME)_3][U(CH_2SiMe_3)_5]$ (2). To a cold, stirring solution (−25 °C) of $LiCH_2SiMe_3$ (4.11 mL, 4.11 mmol, 1.0 M in pentane) in Et_2O (3 mL) was added a solution of UCl_4 (0.312 g, 0.821 mmol) in THF (2 mL) dropwise. The reaction mixture immediately turned green concomitant with the precipitation of a white powder. The solution was filtered through a Celite column (2 cm × 0.5 cm) supported on glass wool, and the solvent was removed in vacuo to provide a bright green solid. The solid was subsequently dissolved in Et_2O (4 mL) and DME (0.5 mL) and filtered through a Celite column supported on glass wool. The filtrate was layered with hexanes (10 mL) and stored at −25 °C for 24 h, resulting in the formation of green crystals. The crystals were washed with hexanes (2 × 2 mL) and dried under vacuum. 0.640 g, 82% yield. Crystals of **2** turned opaque and pale green upon application of vacuum. ^1H NMR (400 MHz, 22 °C, C_6D_6/THF-d_8): δ −2.15 (s, 45H, $CH_2Si\mathit{Me_3}$), 2.98 (s, 18H, DME), 3.16 (s, 12H, DME), 17.80 (br s, 10H, $\mathit{CH_2}SiMe_3$). $^7Li\{^1H\}$ NMR (194 MHz, 22 °C, C_6D_6/THF-d_8): δ −4.96 (s). ^1H NMR (500 MHz, 22 °C, THF-h_8): δ −2.32 (s, 45H, $CH_2Si\mathit{Me_3}$), 3.26 (s, 18H, DME), 3.42 (s, 12H, DME), 16.86 (br s, 10H, $\mathit{CH_2}SiMe_3$). $^7Li\{^1H\}$ NMR (194 MHz, 22 °C, THF-h_8): δ −0.02 (s). Anal. Calcd for $C_{32}H_{85}LiO_6Si_5U$: C, 40.39; H, 9.02. Anal. Calcd for $[Li(DME)_2][U(CH_2SiMe_3)_5]$, $C_{28}H_{75}LiO_4Si_5U$: C, 39.04; H, 8.79. Found: C, 39.16; H, 9.13. UV−vis/NIR (THF, 3.20 mM, 25 °C): 516 (ε = 103 $L \cdot mol^{-1} \cdot cm^{-1}$), 612 ($\varepsilon$ = 65.7 $L \cdot mol^{-1} \cdot cm^{-1}$), 698 ($\varepsilon$ = 37.7 $L \cdot mol^{-1} \cdot cm^{-1}$), 830 ($\varepsilon$ = 21.9 $L \cdot mol^{-1} \cdot cm^{-1}$), 922 ($\varepsilon$ = 25.4 $L \cdot mol^{-1} \cdot cm^{-1}$), 1012 ($\varepsilon$ = 28.2 $L \cdot mol^{-1} \cdot cm^{-1}$), 1042 ($\varepsilon$ = 29.1 $L \cdot mol^{-1} \cdot cm^{-1}$), 1100 ($\varepsilon$ = 25.6 $L \cdot mol^{-1} \cdot cm^{-1}$), 1224 ($\varepsilon$ = 33.4 $L \cdot mol^{-1} \cdot cm^{-1}$), 1394 ($\varepsilon$ = 12.8 $L \cdot mol^{-1} \cdot cm^{-1}$), 1456 ($\varepsilon$ = 12.7 $L \cdot mol^{-1} \cdot cm^{-1}$), 1532 ($\varepsilon$ = 31.5 $L \cdot mol^{-1} \cdot cm^{-1}$), 1892 ($\varepsilon$ = 75.2 $L \cdot mol^{-1} \cdot cm^{-1}$).

$[Li(THF)_4][U(CH_2{}^tBu)_5]$ (3). To a cold, stirring solution (−25 °C) of $LiCH_2{}^tBu$ (0.333 g, 4.27 mmol) in Et_2O (3 mL) was added a solution of UCl_4 (0.320 g, 0.843 mmol) in THF (2 mL) dropwise. The reaction mixture immediately turned dark orange concomitant with the formation of a white powder. The solution was filtered through a Celite column (2 cm × 0.5 cm) supported on glass wool, and the solvent was removed in vacuo to provide a dark orange solid. This solid was subsequently dissolved in Et_2O (4 mL) and filtered through a Celite column supported on glass wool. The filtrate was layered with hexanes (10 mL) and stored at −25 °C for 24 h resulting in the formation of dark orange crystals. The crystals were washed with hexanes (2 × 2 mL) and dried under vacuum. 0.548 g, 73% yield. Crystals of **3** turned opaque upon application of vacuum. ^1H NMR (500 MHz, 22 °C, THF-d_8): δ 2.77 (s, 45H, $CH_2C\mathit{Me_3}$), 26.44 (s, 10H, $\mathit{CH_2}CMe_3$). $^7Li\{^1H\}$ NMR (194 MHz, 22 °C, THF-d_8): δ 0.15 (s). Anal. Calcd for $C_{41}H_{87}LiO_4U$: C, 55.38; H, 9.88. Anal. Calcd for $[Li(THF)_2][U(CH_2{}^tBu)_5]$, $C_{33}H_{71}LiO_2U$: C, 53.20; H, 9.63. Found: C, 53.56, H, 9.93. UV−vis/NIR (THF, 5.22 mM, 25 °C): 622 (ε = 85.2 $L \cdot mol^{-1} \cdot cm^{-1}$), 704 ($\varepsilon$ = 52.1 $L \cdot mol^{-1} \cdot cm^{-1}$), 826 ($\varepsilon$ = 35.5 $L \cdot mol^{-1} \cdot cm^{-1}$), 916 ($\varepsilon$ = 33.4 $L \cdot mol^{-1} \cdot cm^{-1}$), 966 ($\varepsilon$ = 35.3 $L \cdot mol^{-1} \cdot cm^{-1}$), 992 ($\varepsilon$ = 34.0 $L \cdot mol^{-1} \cdot cm^{-1}$), 1052 ($\varepsilon$ = 36.3 $L \cdot mol^{-1} \cdot cm^{-1}$), 1098 ($\varepsilon$ = 32.8 $L \cdot mol^{-1} \cdot cm^{-1}$), 1222 ($\varepsilon$ = 32.3 $L \cdot mol^{-1} \cdot cm^{-1}$), 1412 ($\varepsilon$ = 16.7 $L \cdot mol^{-1} \cdot cm^{-1}$), 1532 ($\varepsilon$ = 34.6 $L \cdot mol^{-1} \cdot cm^{-1}$), 1904 ($\varepsilon$ = 46.0 $L \cdot mol^{-1} \cdot cm^{-1}$).

$[Li(TMEDA)]_2[UMe_6]$ (4). To a cold, stirring solution (−25 °C) of MeLi (0.48 mL, 1.44 mmol, 3.0 M in diethoxymethane) and TMEDA (0.25 mL) in Et_2O (3 mL) was added a solution of UCl_4 (0.090 g, 0.238 mmol) in THF (1 mL) dropwise. The reaction mixture immediately turned orange concomitant with the deposition of a white powder. The solvent was quickly removed in vacuo affording an orange solid. The solid was dissolved in cold Et_2O (5

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Table 1. X-ray Crystallographic Data for Complexes **1**, **3**, **4**, and **5**

	1	**3**	**4**	**5**
empirical formula	$C_{68}H_{163}ClLi_{14}O_{12}Si_5U$	$C_{41}H_{87}LiO_4U$	$C_{18}H_{50}Li_2N_4U$	$C_{104}H_{124}K_4O_5U_2$
crystal habit, color	block, bright green	block, orange	plate, orange	irregular, dark red
crystal size (mm^3)	0.43 × 0.35 × 0.10	0.50 × 0.40 × 0.25	0.30 × 0.20 × 0.05	0.40 × 0.35 × 0.15
crystal system	orthorhombic	monoclinic	orthorhombic	monoclinic
space group	$P2_12_12_1$	$P2_1/m$	$Pbca$	$P2_1/c$
volume (Å^3)	10149(1)	2379.0(5)	5460(1)	9440(1)
a (Å)	10.9396(8)	10.4778(1)	13.945(2)	34.548(2)
b (Å)	28.544(2)	16.944(2)	15.312(2)	14.533(1)
c (Å)	32.502(2)	13.775(2)	25.567(3)	19.188(1)
α (deg)	90	90	90	90
β (deg)	90	103.390(2)	90	78.504(2)
γ (deg)	90	90	90	90
Z	4	2	8	4
formula weight (g/mol)	1684.07	889.18	574.53	2086.62
density (calculated) (Mg/m^3)	1.102	1.171	1.398	1.462
absorption coefficient (mm^{-1})	1.728	3.441	5.952	3.654
F_{000}	3552	820	2272	4160
total no. reflections	82 136	19 784	43 084	79 726
unique reflections	21 304	5067	5746	17 377
final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0488$, $wR_2 = 0.0928$	$R_1 = 0.0534$, $wR_2 = 0.1377$	$R_1 = 0.0568$, $wR_2 = 0.1290$	$R_1 = 0.0976$, $wR_2 = 0.2363$
largest diff. peak and hole (e$^-$Å^{-3})	1.734 and −0.916	2.725 and −2.639	2.586 and −1.455	4.529 and −2.941
GOF	0.923	1.106	1.075	1.121

mL) and filtered through a Celite column (2 cm × 0.5 cm) supported on glass wool, and the volume of the solution was subsequently reduced to 2 mL in vacuo. Storage of the solution at −25 °C for 12 h resulted in the deposition of orange crystals, which were washed with cold hexanes (2 × 2 mL) and dried under vacuum. 0.052 g, 38% yield. ^{1}H NMR (500 MHz, −25 °C, THF-d_8): δ −19.92 (br s, 18H, *Me*), 2.25 (br s, TMEDA), 2.30 (br s, TMEDA). ^{7}Li{^{1}H} NMR (194 MHz, −25 °C, THF-d_8): δ 7.72 (br s).

$\{[K(THF)]_3[K(THF)_2][U(CH_2C_6H_5)_6]_2\}_x$ (5). To a cold, stirring solution (−25 °C) of $KCH_2C_6H_5$ (0.213 g, 1.64 mmol) in THF (2 mL) was added a solution of UCl_4 (0.103 g, 0.271 mmol) in THF (2 mL) dropwise. The reaction mixture immediately turned dark red. The solution was filtered through a Celite column (2 cm × 0.5 cm) supported on glass wool. The filtrate was layered with hexanes (10 mL) and stored at −25 °C for 1 week resulting in the formation of dark red crystals. The crystals were washed with hexanes (3 × 2 mL) and dried under vacuum. 0.198 g, 70% yield. Crystals of **5** turned opaque upon application of vacuum. ^{1}H NMR (500 MHz, 22 °C, C_6D_6/THF-h_8): δ −25.88 (br s, 12H, $CH_2C_6H_5$), 2.87 (br s, 18H, *m*- and *p*-CH), 7.36 (br s, 12H, *o*-CH). ^{1}H NMR (500 MHz, 22 °C, THF-h_8): δ −25.08 (br s, 12H, $CH_2C_6H_5$), 2.69 (s, *p*-CH), 2.92 (s, *m*-CH), 7.44 (br s, 12H, *o*-CH). Anal. Calcd for $C_{104}H_{124}K_4O_5U$: C, 59.86; H, 6.00. Found: C, 56.24; H, 5.28. Samples of **5** consistently analyzed low in carbon content, possibly due to loss of THF on standing. UV−vis/NIR (THF, 3.30 mM, 25 °C): 690 (ε = 260.2 L·mol^{-1}·cm^{-1}), 828 (ε = 63.1 L·mol^{-1}·cm^{-1}), 900 (ε = 59.9 L·mol^{-1}·cm^{-1}), 1000 (ε = 54.2 L·mol^{-1}·cm^{-1}), 1080 (ε = 64.7 L·mol^{-1}·cm^{-1}), 1112 (ε = 60.4 L·mol^{-1}·cm^{-1}), 1188 (ε = 50.5 L·mol^{-1}·cm^{-1}), 1408 (ε = 26.3 L·mol^{-1}·cm^{-1}), 1582 (ε = 26.6 L·mol^{-1}·cm^{-1}), 2034 (ε = 111 L·mol^{-1}·cm^{-1})

X-ray Crystallography. Data for **1**, **3**, **4**, and **5** were collected on a Bruker 3-axis platform diffractometer equipped with a SMART-1000 CCD detector using a graphite monochromator with a Mo Kα X-ray source (α = 0.710 73 Å). A sample-to-detector distance of 4.950 cm was used for **1**, **3**, and **4**, whereas a distance of 6.950 cm was used for **5**. The crystals were mounted on a glass fiber under Paratone-N oil, and all data were collected at 150(2) K using an Oxford nitrogen gas cryostream system. A hemisphere of data was collected using ω scans with 0.3° frame widths. Frame exposures of 20, 12, 25, and 15 s were used for complexes **1**, **3**, **4**, and **5**, respectively. Data collection and cell parameter determination were conducted using the SMART program.[108] Integration of the data frames and final cell parameter refinement were performed using SAINT software.[109] Absorption correction of the data was carried out empirically based on reflection ψ-scans. Subsequent calculations were carried out using SHELXTL.[110] Structure determination was done using direct or Patterson methods and difference Fourier techniques. All hydrogen atom positions were idealized and rode on the atom of attachment with exceptions noted in the subsequent paragraph. Structure solution, refinement, graphics, and creation of publication materials were performed using SHELXTL.[110]

Structure **3** exhibits positional disorder of the neopentyl ligands. The positional disorder was addressed by modeling the molecule in two orientations, and occupancy of each orientation was determined through data refinement. Additionally, a disordered THF molecule was modeled in two positions with occupancies of 0.5 each. Idealized hydrogens were not assigned to the disordered carbon atoms. Structure **5** possessed a minor twin component, present in the analysis of several samples, which could not be resolved. A summary of relevant crystallographic data for **1**, **3**, **4**, and **5** is presented in Table 1.

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Supporting Information Available: X-ray crystallographic details (as CIF files) of **1**, **3**, **4**, and **5**; Selected NMR spectra of **1**−**5**. Magnetic susceptibility plots for **2**, **3**, **5**, and $[Li(THF)]_2[U(O^tBu)_6]$. This material is available free of charge via the Internet at http://pubs.acs.org.

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