### Achievements in Uranium Alkyl Chemistry: Celebrating Sixty Years of Synthetic Pursuits

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Achievements in Uranium Alkyl Chemistry: Celebrating Sixty Years of Synthetic Pursuits

Sara A. Johnson* and Suzanne C. Bart*

Organouranium complexes containing uranium-carbon σ-bonds have been highly sought since initial exploration of these complexes during the 1950’s. Since this time, a variety of uranium starting materials have been developed and alkylating reagents used in order to generate such species. Trivalent uranium alkyl compounds have recently moved past using the bis(trimethylsilyl)methyl ligand with the use of larger ancillary hydrotris(pyrazolyl)borate ligands. The uranium(IV) congeners are dominated by cyclopentadienyl ligands, but recent developments have shown that amide, alkoxide, and phosphines are also suitable ligand frameworks for supporting such species. A family of uranium(IV) species that have been formed via cyclometallation and neutral homoleptics have also been described. Highly reactive uranium(V) and (VI) alkyl complexes have also recently been synthesized at low temperatures. The representative studies presented herein have helped to pioneer the field of organouranium alkyl chemistry.

1. Introduction

Organouranium complexes, those containing uranium-carbon bonds, have been sought after since the middle of the last century, as the presumed increased volatility of these species was potentially useful to facilitate uranium isotope separation. Compounds containing uranium-carbon σ-bonds were especially desirable, as these ligands conferred such volatility to transition metal derivatives, and were previously unexplored for the actinide elements. Uranium alkyls specifically were explored during the pre-WWII era, prior to the start of the Manhattan project. In 1956, Gilman reported that initial attempts at the synthesis of “simple organometallic derivatives, such as tetramethyluranium, if they existed at all, were extremely unstable, and their isolation offered little chance of success.” From these early studies came the perception that uranium alkyl species were inherently unstable. Thus, efforts were focused on oxygen, nitrogen, and sulfur linkages to uranium, in hopes that these would be more robust.

It wasn’t until the 1970’s with the studies of Marks, who generated the first family of thermally stable σ-type uranium-carbon bonds, Cp₂UR, did the opinion of uranium alkyl species begin to change. The stability of the Cp₂UR family was attributed to the coordinative saturation imparted by the tris(cyclopentadienyl) framework, which prevented expansion of the coordination sphere due to β-hydrogen elimination. Using substituted cyclopentadienides provided enough steric protection for in-depth exploration of the metalloocene framework for uranium, facilitating the synthesis of bis(cyclopentadienyl)uranium alkyl derivatives for comparison to their transition metal counterparts.

Concurrent with these early discoveries were studies aimed at synthesizing neutral homoleptic uranium tetra(alkyl)s. Homoleptic compounds are typically difficult to synthesize due to the lack of bulky ancillary ligands commonly used to protect the reactive metal centre. Building on the Gilman work, Marks and Seyam demonstrated such species could be made at low temperatures, but these “UR₄” compounds quickly decomposed during warming, precluding their use as general starting materials for organouranium synthesis. It wasn’t until Wilkinson and Sigurdson isolated a family of homoleptic uranates of the form [Li(solvent)]₃[UR₆] that uranium alkyls were isolated in the absence of ancillary ligands.

Uranium alkyls remain an area of interest due to the broad use of their transition metal counterparts in catalytic applications. Distinct advantages come with the actinide system that warrant continued study, including the large ionic radius of uranium that can accommodate high coordination numbers, larger substrates, and multiple active sites per metal centre. Additionally, these U-C σ-bonds provide the opportunity to examine f orbital involvement and covalency in actinide bonding studies, which are typically performed for species with uranium-element multiple bonds.

The fundamental discoveries discussed in this Perspective pioneered the field of σ-bonded uranium alkyls, carrying us from initial thoughts of instability, past derivatization of uranium tetrachloride with alkyl lithium reagents, to realization of alkyl species in a variety of oxidation states and coordination environments. The generation and availability of new uranium...
starting materials, alkylating reagents, and synthetic capabilities has opened this area, allowing for the formation of previously unisolable or unobserved alkyl uranium species. Herein, we summarize significant developments in the field of α-bonded uranium alkyls, as well as representative examples of significant molecules in their time. Uranium-carbon bonds with π character, such as ylides and arenes, are beyond the scope of this review, as are significantly stronger α-donors, such as N-heterocyclic carbenes, carbon monoxide, and isocyanides. Synthetic strategies that consider reagents, solvent combinations, temperatures and reaction by-products are highlighted. Where possible, notable characterization and reactivity are also included. The examples chosen are organized by oxidation state, followed by ancillary ligand type, with subsequent discussion of homoletic compounds.

2. Uranium(III) Alkyls

Synthesis of trivalent uranium σ-alkyls has proven to be a difficult endeavor as compared to those in higher oxidation states. Initial challenges stemmed from the lack of commonly available uranium(III) starting materials, whereas more recent studies have found these complexes to be unstable, complicating characterization at ambient temperature. The discoveries of $\text{UI}_3(\text{THF})_4^{10}$ and its recent relative, $\text{UI}_3(\text{dioxane})_2$, have provided a convenient platform for such studies. Using bulky alkyl substituents, coordinating solvents and large ancillary ligands has also aided in the synthesis of uranium(III) centres containing U-C α-bonds.

2.1 Cp Derivatives: The sterically bulky 1,2,3,4,5-pentamethylcyclopentadienide (Cp*) supporting ligand was successfully used to generate the first uranium(III) σ-alkyl compound, $\text{Cp}^\ast\text{U}+\text{CHSiMe}_3$ (1). Marks and co-workers discovered that treating the uranium(III) chloride trimer, $[\text{Cp}^\ast\text{U}+\text{Cl}]_3$, with LiCHSiMe$_3$ in diethyl ether at room temperature afforded the desired product with loss of LiCl (Figure 1). The diethyl ether facilitates salt metathesis by acting as a coordinating solvent to dissociate the trimer and serving to stabilize the monomeric uranium(III) intermediate. Although no crystallographic data were obtained, solution molecular weight experiments established $\text{Cp}^\ast\text{U}+\text{CH}+\text{SiMe}_3$ as a monomer. Hydrogenation of $\text{Cp}^\ast\text{U}+\text{CH}+\text{SiMe}_3$ results in formation of the trivalent monohydride dimer, $[\text{Cp}^\ast\text{U}+\text{H}]_2$. Similarly, Evans and co-workers showed successful alkylation of the sterically crowded $[\text{Cp}^\ast\text{U}+\text{Cl}]_2(\mu-\text{n}=\text{C}_6\text{H}_5)$ sandwich complex, which has a bridging reduced benzene ring, using the same reagent. Alkylation in toluene at -35 °C occurred with loss of LiCp*, forming the dimeric uranium sandwich complex, $[\text{Cp}^\ast\text{U}+\text{CHSiMe}_3]_2(\mu-\text{n}=\text{n}=\text{C}_6\text{H}_5)$ (2) (Figure 1). A resonance assignable to the methine proton was not visible in the $^1\text{H}$ NMR spectrum, but crystallographic data confirmed the structure, with a U-C$_\text{alkyl}$ distance of 2.508(2) Å.

In 1986, Folcher and co-workers reported that $\text{Cp}_3\text{U}^\ast\text{Bu}$ could be reduced to a family of uranium(III) alkyl anions, $[\text{Cp}_3\text{U}^\ast\text{Bu}]^{-}$, by treatment with one equivalent of LiR (R = "Bu (3), Me (4), Ph (5)) (eq. 1). In the cases of red-brown 3 and dark brown 4, gas chromatographic analysis revealed evolution of butane for both with methane also detected for 4 as the reaction proceeds. To make 5, PhLi was added to $\text{Cp}_3\text{U}^\ast\text{Bu}$ in diethyl ether/benzene, therefore benzene loss could not be detected. $^1\text{H}$ NMR spectroscopic data (benzene-d$_6$) showed the formation of the uranium(III) alkyl anion in each case, with resonances visible for the $^6\text{Bu}$ in 3 (98.5 (2H), 15.8 (2H), 14.0 (2H), 12.0 (3H) ppm), CH$_3$ in 4 (101 ppm), and Ph in 5 (11.3 (2H), -5.2 (2H), -3.3 (1H) ppm). Crystals of 3 suitable for X-ray crystallography were grown by slow diffusion of solutions of $[\text{Cp}_3\text{U}^\ast\text{Bu}]^{-}[\text{Li}]$ and $\text{CP}_4\text{H}_2\text{N}_2\text{O}_4$ (2.1.1 cryptand) through scinted glass. Data showed a distorted tetrahedral uranium centre with a U-C σ bond of 2.557(9) Å and U-C-C angle of 120(1)° (Figure 2). The neutral uranium(IV) starting material, $\text{Cp}_3\text{U}^\ast\text{Bu}$, has a shorter U-C$_\text{alkyl}$ distance of 2.426(23) Å than 3, explained by the difference in ionic radius between U(III) and U(IV) anions (0.1 Å).
smaller than –CH(SiMe₃)₂ on uranium possible. Recently, a family of trivalent alkyls of the form Tp*UR (R = CH₂Ph (6), CH₂SiMe₃ (7), CH₃ (8), ³⁵Bu (9)) was synthesized via salt metathesis with KCH₂Ph, NaCH₂SiMe₃, NaMe or Na³⁵Bu in THF at -35°C (eq. 2), respectively, eliminating KI or NaI. Grignard reagents were unsuccessful in the formation of 6-9, instead producing the halide exchange product. Characterization by Ï€H NMR spectroscopy (benzene-d₆) showed upfield shifted protons on the α-carbon for 6 at 21.35 ppm, for 7 at 64.03 ppm, and for 8 at 66.64 ppm, less shifted than those for 3 and 4. Compound 9 is not stable at ambient temperature, thus Ï€H NMR data collected at -15°C (toluene-d₈) showed a methylene resonance at 73.52 ppm, consistent with those reported for 6-8. Crystallographic characterization of 6-8 showed seven coordinate uranium centres with increasing U-C bond distances of 2.54(3) Å (CH₃), 2.57(2) Å (CH₂Ph), and 2.601(9) Å (CH₂SiMe₃) that are on the order of those in 4 and track with increasing steric of the alkyl group. A magnetic moment (23°C) of 2.6 μₜ were measured for compounds 7 and 8, while that of 6 was found to be 2.5 μₜ. Compound 6 readily undergoes insertion of CO₂ or CS₂ to generate the respective uranium(III) carboxylate, Tp*U(κ²-O₂CCH₂Ph), and thiocarboxylate, Tp*U(κ²-S₂CCH₂Ph). The U-C α-bond in 6 is easily protonated with terminal alkynes, amines, and thiol to generate the corresponding uranium(III) family, Tp*UX (X = CCPh, CCSiMe₃, NHPh, NHCH₂Ph, SPh). In the presence of organoazides or diazoalkanes, 6 reacts to form the oxidized uranium(IV) imido complexes, Tp*UNR (R = Mes, Ph, Ad). Hydrazino complexes, Tp*U(η²-N₂CPh₂) and Tp*U(η²-N₂CHSiMe₃), with loss of benzyl radical that subsequently couples and is identified as benzyl.

The Tp* ligand also supports the uranium(III) dialkyl, Tp*U(CH₃Ph₂)(THF) (10), whose synthesis is achieved by addition of KCH₂Ph to Tp*UL₂(THF)₂ in THF at -35°C, with loss of KI (eq. 3). Identification by Ï€H NMR spectroscopy (THF-d₈) showed a resonance for the equivalent methylene protons at 0.04 ppm. The U-C α-bonds of 2.615(7) and 2.604(9) Å are on the order of those observed for 7, and slightly longer than for 3, 6, or 8, likely due to the steric crowding from the two η⁴-coordinated benzyl rings (Figure 2). Exposure of 10 to hydrocarbon solvents results in decomposition due to loss of the coordinated Lewis base. Attempts to form Tp*U(CH₂SiMe₃)₂ with LiCH₂SiMe₃ under the same conditions resulted in isolation of [Li(THF)₂]Tp*UL₂, presumably due to side reactions with eliminated Li(THF) that is soluble in THF (eq. 3). As is the case for 6, mesityl azide oxidizes 10, forming the uranium(IV) alkyl imido species, Tp*U(NMes)CH₂Ph, and half and equivalent benzyl, again indicating benzyl radical extrusion.

![Figure 2. Solid state structures of uranium(III) alkyls: Folcher’s [Cp₂U⁻Bu]²⁻ (left), Bart’s Tp*U(CH₂Ph)₂(THF) (10) (centre), Sattelberger’s U(CH₂Me)₃ (11) (right). The lithium counter ion in 3 has been removed for clarity.](image)

**Eq. 3.** Salt metathesis reactions of Tp*UL₂(THF)₂ (10).

2.3 Homoleptic alkyls: Synthesis of a uranium(III) homoleptic alkyl was accomplished by Sattelberger and co-workers, using the same large bis(trimethylsilyl)methyl group found successful by Marks and Evans. Treating U(O-2,6-²Bu₂Ph)₃ with three equivalents of LiCH₂SiMe₃ in hexanes at room temperature for 2 hours afforded U(CH₂SiMe₃)₃ (11). The eliminated aryl oxide, LiO-2,6-²Bu₂Ph, is soluble in hexane, facilitating separation from the desired organouranium species by repeated washing. As in the case for [Cp*(CH₂SiMe₃)₂]U₂(μ-η³-η⁴-C₆H₄), the Ï€H NMR spectrum (benzene-d₈) showed no resonance for the methine bonded to uranium. Characterization by X-ray crystallography showed a trigonal pyramidal uranium(III) centre, with a U-C distance of 2.48(2) Å, which is in range of uranium(III) complexes supported by ancillary ligands (Figure 2). The uranium centre is removed from the plane of the three carbon atoms by 0.90 Å. The pyramidal bonding in 11 was explored computationally with the model complex U(CH₂Ph)₃, and found to be due to the contribution of the uranium 6d orbitals, rather than 5f orbitals, in the uranium-carbon bonds. The solid state structure also shows three γ-agostic interactions to trimethylsilyl hydrogens.
Although stable at room temperature, 11 decomposes around 60° C, most likely due to \( \gamma \)-hydrogen abstraction. Magnetic studies from 100 – 270 K revealed a \( \mu_{\text{eff}} = 3.0 \, \mu_B \), comparable to that observed in U(\( \eta^5 \)-SiMe\( _\text{3} \))\( \text{Cp}^* \),\( ^{31} \) and higher than those for 6-8. Addition of HO-2,6-\( \text{Bu}_3\text{Ph} \) to 11 regenerated the uranium tris(aryl oxide) starting material. Traditional reaction pathways through salt metathesis using UCl\( _3 \)(THF)\( _2 \) and LiCH(SiMe\( _\text{3} \))\( \text{Cp}^* \) did not give the desired product, but similarly to the chemistry with Tp\(^*\), produced the lithium ‘ate’ complex, [Li(THF)]\( \text{UCl(CH(SiMe}_3)} \)\( _2 \)\( _3 \)] from reaction of the alkyl species with LiCl.

3. Uranium(IV) Alkyls

Tetravalent uranium alkyls have been heavily explored since the inception of organouranium chemistry, due to the availability and stability of uranium tetrachloride, an easy to make and handle precursor that readily undergoes salt metathesis reactions. The thermodynamic stability of this oxidation state has provided a platform that has supported extensive study of alkyls, making this the largest category to date.

3.1 Cyclopentadienyl Derivatives: Unsubstituted cyclopentadienyl ligands were initially used to generate a family of stable, uranium(IV) alkyls as reported by Marks and co-workers. Treating a suspension of Cp\(_2\)UCl in diethyl ether with three equivalents of LiR (R = Me (12), \( \text{Bu}_3\) allyl (13), neopentyl (14), C\(_5\)F\(_5\), \( \text{Pr}^\text{r} \)) or MgXR (R=CH\(_3\)C(CH\(_2\))\(_2\)),\( ^{12} \) \( \text{Bu}_3\),\( ^7 \) cis-2-but enyl,\( ^7 \) trans-2-but enyl,\( ^7 \) Ph,\(^7 \) vinyl (15)\( ^7 \)) at -78° C afforded the desired products after warming to room temperature, stirring for 2 hours, and filtration to remove the LiCl or magnesium salts. \(^1\)H NMR spectroscopic measurements (benzene-\( d_6 \)) confirmed product formation. Compared to uranium(III) alkyls, the chemical shifts reported for protons on the \( \alpha \)-carbon of uranium(IV) alkyls appear downfield. For example, resonances for the protons on sp\(^2\)hybridized \( \alpha \)-carbons range from 186 (14) to 202 ppm (12), while that for the proton on the sp\(^2\) \( \alpha \)-carbon in 15 appears at 163.3 ppm. The allyl ligand in 13 undergoes a \( \alpha/\pi \) conversion on the NMR timescale, causing a shift in the single resonance for the equivalent \( \alpha \)-protons to 126 ppm.

Bis(cyclopentadienyl) uranium alkyl species have also enjoyed thorough study, due in part to their analogy with transition metal metallocenes. Pivotal to the development of such compounds is the variation in coordination environments at the uranium centre that can be obtained by steric tuning of the cyclopentadienyl. Substituted cyclopentadienides, such as the pentamethyl variant (Cp\(^*\)), provide the required steric protection for the large uranium(IV) ion preventing common alkyl decomposition and ligand scrambling pathways.

With the goal of manipulating coordinative unsaturation for optimum chemical reactivity, Marks and co-workers generated Cp\(^*\)\(_2\)UMe\(_2\) (16), the first member of the uranium(IV) dialkyl family, produced by addition of 2 equivalents of MeLi to a diethyl ether suspension of Cp\(^*\)\(_2\)UCl\(_2\) at -78° C, followed by filtration to remove LiCl and recrystallization in toluene (eq. 4).\(^{33} \) As an organoaactinide species that was chemically reactive and versatile, 16 also provided a direct chemical comparison to transition metal analogues (Ti, Zr).\(^{34,36} \) Compound 16 is more stable than previous U(IV) alkyls, with a half life of ~16 hrs in toluene at 100° C. Identification of 16 was possible by \(^1\)H NMR spectroscopy (benzene-\( d_6 \)), which showed a resonance at -124 ppm assignable to the two equivalent uranium methyl groups. This is far upfield from those observed for the tris(cyclopentadienyl) congeners and uranium(III) compounds. The monomeric nature of 16 was described in the initial report, and was confirmed by cryoscopic molecular weight measurements.\(^{33} \)

The isolation of 16 was significant as it demonstrated that uranium dialkyls can be stable, in contrast to previous attempts that gave data showing otherwise (\textit{vide infra}). The Cp\(^*\) ligands protect the uranium-methyl groups but also allow reactivity with dihydrogen, generating isolable uranium hydride species.\(^{37} \) Compound 16 has enhanced reactivity towards small molecules as compared to its Group (IV) analogues due to its larger ionic radius and higher degree of coordinative unsaturation. The molecular structure of 16 was determined by Kiplinger and co-workers in 2004, which confirmed the monomeric nature of 16 with U-C \( \sigma \) bonds of 2.424(7) and 2.414(7) \( \text{Å} \), and a C-U-C angle of 94.5(3)\(^\circ\).\(^{38} \) The bond distances in 16 are shorter than those in trivalent uranium alkyls as would be expected. Structural data were simultaneously determined by Eisen and co-workers.\(^{39} \)

With the isolation of Cp\(_2\)UMe\(_2\), additional members of the dialkyl family, Cp\(_2\)U(CH\(_2\)SiMe\(_3\))\(_2\),\(^{37} \) Cp\(_2\)U(\( \text{CH}_2\)Ph)\(_2\),\(^28 \) Cp\(_2\)UPh\(_2\),\(^37 \) were soon synthesized by similar procedures. The monoaalkyl variants, Cp\(^*\)\(_2\)URCI, were made using only one equivalent of LiR in toluene.\(^{37} \) Bis(cyclopentadienyl) uranium(IV) dimethyl compounds were isolated with variations in the cyclopentadienyl ring as well, including Cp\(_2\)\(_2\)UMe\(_2\) (Cp\(_2\)\(_2\)) = \( \eta^5\)-1,3-(SiMe\(_3\))\(_2\)C\(_6\)H\(_3\))\(^{30} \), Cp\(_2\)UMe\(_2\) (Cp\(_2\)) = \( \eta^6\)-1,3-(CMe\(_3\))\(_2\)C\(_6\)H\(_3\))\(^{30} \) and (Cp\(_{\text{5-bl}}\))\(_2\)UMe\(_2\) (Cp\(_{\text{5-bl}}\)) = \( \eta^1\)-1,2,4-(Me\(_2\)C\(_2\))\(_2\)C\(_6\)H\(_3\)) using the same experimental conditions. Evans and co-workers synthesized Cp\(_{\text{5-bl}}\)\(_2\)UCl\(_2\) with MeLi, followed by stirring for 10 hours and centrifugation to remove...
LiCl and black insoluble solids.\textsuperscript{41} (Cp\textsubscript{Me4SiMe3})\textsubscript{2}UMe\textsubscript{2} (Cp\textsubscript{Me4SiMe3} = \textgreek{n}\textacuted{C}\textsubscript{2}Me\textsubscript{3}SiMe\textsubscript{3}) was synthesized similarly from (Cp\textsubscript{Me4SiMe3})\textsubscript{2}UCl\textsubscript{2} and MeLi, but required a reaction time of 12 hours. Kiplinger and co-workers synthesized Cp\textsubscript{Me4Et}\textsubscript{2}UMe\textsubscript{2} (Cp\textsubscript{Me4Et} = \textgreek{n}\textacuted{C}\textsubscript{2}Me\textsubscript{2}Et) by treating a diethyl ether/dioxanes solution of Cp\textsubscript{Me4Et}\textsubscript{2}UCl\textsubscript{2} with MeMgBr dropwise, followed by stirring for 16 hours and filtration to remove magnesium salts.\textsuperscript{42}

\textsuperscript{1}H NMR spectroscopic and structural data for the family of bis(Cp\textsuperscript{5}) uranium dimethyl compounds are presented in Table 1. The chemical shift of the resonance assignable to the protons of the uranium-methyl ranges from -21 to -138 ppm, tracking with the electron donating ability of the cyclopentadienyl substituent. The most electron donating ring, Cp\textsubscript{Me4Et}, has the resonance with the largest upfield shift. Replacing the ethyl with a methyl decreases the electron donation, causing a downfield shift in the resonance that continues down the series to the tetra- and disubstituted ligands, which are substantially less electron releasing. The chemical shift trend correctly shows that the bis(trimethylsilyl) cyclopentadienyl ring is less electron donating than its butyl congener. The U-C bond distances for the methyl groups range from 2.37(3) to 2.429(4) \textgreek{A}, serving as a reference value for other uranium(IV)-C\textsubscript{alkyl} bonds.

Table 1. Spectroscopic and structural data for Cp\textsubscript{2}UMe\textsubscript{2} derivatives.

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<th>Compound</th>
<th>U-CH\textsubscript{3} Resonance \textsuperscript{1}H NMR Spectroscopy (ppm)</th>
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<td>Cp\textsuperscript{4}UMe\textsubscript{2}</td>
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Isolation of the uranium(IV) trialkyl, Cp*U(CH\textsubscript{2}Ph\textsubscript{3}), was recently performed by reaction of Cp*UCl\textsubscript{2} and LiCH\textsubscript{2}Ph in THF at -78° C\textsuperscript{43} or from \textit{in situ} reaction of UCl\textsubscript{4} and MgClCp* in toluene/dioxanes at ambient temperature, followed by addition of 3 equivalents of MgCl(CH\textsubscript{2}Ph).\textsuperscript{44} Similarly, the (Cp\textsuperscript{3}U)\textsubscript{2}UR (Cp\textsuperscript{3} = \textgreek{n}\textacuted{C}\textsubscript{2}Me\textsubscript{3}SiH\textsubscript{2}; R=Me, \textgreek{Bu}, CH\textsubscript{2}SiMe\textsubscript{3}, CH\textsubscript{2}Ph, CCPh, CHCH\textsubscript{2}) family was synthesized in an analogous fashion with alkyl lithium reagents.\textsuperscript{45}

The alkyl groups in these Cp-based uranium alkyl compounds are subject to further reactivity. For instance, the benzyl groups in Cp*U(CH\textsubscript{2}Ph)\textsubscript{3} readily undergo protonation, thus adding 2 equivalents of cyclopentadienyl yields the mixed Cp compound, Cp*CP(U(CH\textsubscript{2}Ph), and two equivalents of toluene.\textsuperscript{46} Methyl abstraction can be accomplished by treating a toluene solution of Cp*\textsubscript{2}UMe\textsubscript{2} with BPh\textsubscript{3}, forming [Cp*\textsubscript{2}UMe\textsubscript{2}]BPh\textsubscript{3}.\textsuperscript{46} Subsequent addition of KCp, Cp*\textsuperscript{4}, or KCp*\textsuperscript{4} generates the tris(cyclopentadienyl) uranium(IV) alkyls, Cp*\textsubscript{2}CpUMe\textsubscript{2}, Cp*\textsubscript{3}UMe\textsubscript{2}, or Cp*\textsubscript{2}Cp*\textsubscript{2}UMe\textsubscript{2}, respectively (eq. 4).\textsuperscript{47} The U-C bonds in 16 are subject to insertion chemistry, as in the case of diazoalkanes, which generates uranium(IV) bis(hydrazonato) complexes, Cp*\textsubscript{2}U[\textgreek{n}(N-N')=R-N-N'=CPh\textsubscript{2}]\textsubscript{2} (R = CH\textsubscript{3}, PhCH\textsubscript{2}).\textsuperscript{48}

Eq. 4. Synthesis of Cp*\textsubscript{2}UMe\textsubscript{2} (16) and Cp*\textsubscript{3}UMe

3.2 Non-Cp Systems: From the seminal examples of cyclopentadienyl ligands in early organouranium chemistry comes more recent studies focusing on a variety of non-Cp based ligands. These scaffolds take advantage of strong anionic heteroatom-uranium \textalpha-bonds to prevent ligand dissociation, facilitating installation of alkyl substituents on the uranium ion.

Amides have proven popular ligands for organouranium species. For example, Cummins and co-workers reported that adding a thawing diethyl ether solution of MeLi (1.1 equivalents) to a frozen solution of the uranium tris(amide) compound, ((3,5-Me\textsubscript{2}C\textsubscript{2}H\textsubscript{4}N\textsubscript{5}Bu\textsubscript{3})\textsubscript{3}U, affords ((3,5-Me\textsubscript{2}C\textsubscript{2}H\textsubscript{4}N\textsubscript{5}Bu\textsubscript{3})UCH\textsubscript{3} (17) (Figure 4)). Isolation is possible after stirring for one hour at room temperature followed by pentane extraction and filtration to remove Li\textsubscript{2}.\textsuperscript{49} Crystallographic characterization showed a U-C distance of 2.466(7) \textgreek{A}, close to that reported for Cp*\textsubscript{2}UMe\textsubscript{2} but shorter than the uranium(III) compounds. Similarly, Behrens et al. used chelating NCN ligands to stabilize uranium(IV) alkyls. To (p-R\textsubscript{2}C\textsubscript{2}H\textsubscript{4}(NSiMe\textsubscript{3})\textsubscript{2})UCl was added an equivalent of MeLi in diethyl ether at -100° C. Warming to room temperature over 12 hours produced tetravalent (p-R\textsubscript{2}C\textsubscript{2}H\textsubscript{4}(NSiMe\textsubscript{3})\textsubscript{2})UMe (R= H (18) (Figure 4), CF\textsubscript{3} (19), OMe (20)) with loss of LiCl.\textsuperscript{50} These derivatives were characterized by mass spectrometry, and resonances for the \textalpha-bonded methyl substituents were visible in the \textsuperscript{1}H NMR spectrum (benzene-\textdelta) at -34.8 (18), -35.9 (20), and -29.6 (19) ppm, upfield of the corresponding uranium(III) derivatives but in line with that of tetravalent Cp*\textsubscript{2}UMe\textsubscript{2}. Analysis of 18 by X-ray crystallography showed a capped octahedral uranium centre, where a triangle face of the distorted octahedron has a methyl cap with a U-C bond distance of 2.498(5) \textgreek{A}. The olive green dimethyl derivative, [(2,4,6-(CF\textsubscript{3})\textsubscript{3}C\textsubscript{6}H\textsubscript{3}(NSiMe\textsubscript{3})\textsubscript{2})UMe\textsubscript{2} was generated by addition of two equivalents of methyl lithium to the corresponding dichloride species at -70° C. Warming to room temperature followed by filtration to remove LiCl afforded the product, which was confirmed by a signal at -29.5 ppm in the \textsuperscript{1}H NMR spectrum for the two equivalent methyl groups, within error of the mono(methyl) derivative.
In 2008, Diaconescu and co-workers began exploring the use of ferrocene diamides, fc(NSiRMe₂)₂, as redox-active supports for uranium(IV) alkyls. Using a cooled suspension of fc(NSiRMe₂)₂U₁₂(THF)₄ in diethyl ether or toluene and treating with 2 equivalents of benzyl potassium and warming to room temperature produced the uranium(IV) dibenzyl compounds, fc(NSiRMe₂)₂UBn₂ (R= Bu (21))53, Ph (22))55. ¹H NMR spectroscopic analysis of 21 showed a far upfield resonance at -154.46 ppm for the methylene protons (benzene-d₆), on the order of those for (Cp₃U)₂UMe₂, whereas those for 22 could not be definitively assigned. Both 21 and 22 were studied by X-ray crystallography, and showed uranium-iron interactions with respective U-Fe distances of 3.1878(5) Å and 3.1874(4) Å, shorter than the sum of the iron and uranium covalent radii (3.28 Å).52 The U-C distances of 2.5153(37) and 2.4827(36) Å for 21 and 2.4781(21) and 2.4648(22) Å for 22 are on the order of those for the bis(cyclopentadienyl) uranium(IV) dimethyl family. Variation of the silyl substituent has little effect, as electronic differences between members of the dibenzyl family (R = Bu, Ph, Me) are small as observed through electrochemical, spectroscopic, and computational experiments.52 Once again, benzyl group protonation occurs upon treating a concentrated toluene solution of 21 with [Et₃NH][BPh₄]. Stirring at room temperature and recrystallizing from toluene and diethyl ether affords the cation-anion pair, [fc(NSiBuMe₂)₂UBn(OEt₂)][BPh₄] (24) (eq. 5). Crystallographic data obtained for 24 showed a pseudotetrahedral uranium centre with an n²-coordinated benzyl group and a U-C_benzyl distance of 2.48 Å. Again, the structural parameters also support communication between the uranium and iron centres (3.08 Å). Magnetic studies confirmed a stronger U-Fe interaction in cationic 24 vs. the parent dibenzyl 21, with a lower overall magnetic moment of 2.4 μₘ for 24 vs. 3.2 μₘ (300 K) for 21.53 This phenomenon is suggested to originate from better U-Fe orbital overlap in 24.51 Compound 21 is an active precatalyst for both intramolecular alkyn hydroamination54 and mediates aromatic heterocycle activation with a variety of substrates.55–58

Both 21 and 23 can be made by in situ reaction of U₂(THF)₄ with 3 equivalents of benzyl potassium, presumably generating U(CH₂Ph)(THF)₂, followed by 0.75 equivalents of fc(HNSiRMe₂)₂ in toluene and diethyl ether at -78°C.59 Variation of the alkyl lithium is possible, thus fc(NSiBuMe₂)₂U(CH₂CH₂Me₂)₂ (25) and fc(NSiBuMe₂)₂U(CH₂CMe₃)₂ (26) have also been isolated. The latter synthetic strategy is effectively applied to the 2,6-bis(2,6-disopropylanilidomethyl)pyridine ligand (NNPy), affording (NNPy)₂U(CH₂Ph)₂, whereas using only 2 equivalents of KCH₂Ph generates the monobenzyl species, (NNPy)(U(CH₂Ph)I. Thus, in situ generation of the trialkyl precursor followed by treating with an ancillary ligand offers a one-pot synthesis for these uranium(IV) dialkyls.

Others have taken advantage of the strong oxophilicity of uranium with the use of alkoxide ligands. Andersen and co-workers treated U(OCH(CH₃)₂)₂ with MeLi (1 equivalent in hexanes) to produce five coordinate LiUCH₂(OCH(CH₃)₂)₂ (27), which features a lithium counterion coordinated to two oxygens (Figure 4).60 Compound 27 shows a square pyramidal geometry in the solid state, with an apical methyl group displaying a U-C distance of 2.465(7) Å, and dissociates readily in solution, generating MeLi and the tetravalent alkoxide starting material. Although the solution and solid state structures are different, a resonance visible at -204 ppm (benzene-d₆) in the ¹H NMR spectrum is assigned as the methyl group σ-bonded to uranium, clearly a resonance shifted farther upfield than all of the neutral uranium(IV) species previously discussed and likely due to the electron rich anion.

Either donors flanked by amides have also proven to be effective ligands to mediate uranium alkyl synthesis. These tridentate NON pincer donors represent an important class due to the ability to easily alter their sterics and electronics. For instance, Leznoff and co-workers have explored derivatives of the (NON) ligand, [[⁺⁻]NON]²⁺ = ([CH₃)₂CN(Si(CH₃)₂)]O and [DOPP]⁻COOCN = (((2,6-Pr₂C₆H₄)N(CH₂CH₂)₂)O. Synthesis of [[⁺⁻]NON]UR₂ (R = CH₃ (28) or CH₃(SiMe₃) (29)) can be achieved either by adding 4 equivalents of MgCl₂/C₅H₅ or LiCH₂SiMe₃ in toluene/THF at

Eq. 5. Protonation of a benzyl group on fc(NSiBuMe₂)₂UBn₂ (21) by [Et₃NH][BPh₄], forming [fc(NSiBuMe₂)₂UBn(OEt₂)][BPh₄] (24).

-78° C to dimeric [(dipeptide)UXCl]2 or by treating (dipeptide)UXLi(THF)2 with 2 equivalents of LiCH2SiMe3 in toluene at -30° C (eq. 6). While no crystallographic evidence could be obtained for either compound, 1H NMR studies confirmed the η1-coordination of the allyl ligand in 28, with the methine resonance appearing at 72.84 ppm (toluene-d5). The positive shift of this resonance is similar to that observed for Cp3U(allyl) (13), but is opposite those of the methyl resonances in the Cp32UMe2 family, which all have negative chemical shift values. The shift of the methylene (-148.9 ppm) protons in 29 is in line with the Cp32UMe2 family. The tetravalent alkyls, (dipeptide)NCOCN)UX2, are synthesized from (dipeptide)UXCl with 2 equivalents of LiCH2SiMe3 (30) or KCH2Ph (31) in toluene at -30° C. The molecular structure of 30 has U-C distance of 2.40(2) and 2.44(2) Å, whereas 31 shows both η1- and η2-coordinated benzylic groups, with respective U-C distances of 2.483(14) and 2.544(13) Å. Resonances for the respective η1- and η2-benzylic methylene protons are observed at -125.92 and -73.46 ppm by 1H NMR spectroscopy (benzene-d6), track with their bond distances, and are on the order of those observed for 29 and 16.

Emslie and co-workers have made use of a rigid NON type ligand, tetraakis-(2,6-diisopropylphenyl)-2,7-di-tert-butyl-9,9-dimethylxanthene = XA2, to stabilize analogous species. To (X2A2UCl)(K(dme))2, 2 equivalents of an alkylilium are added in hexane at -78° C and the reaction mixture warmed to room temperature over 12 hours, producing XA2UX2 (R=CH2SiMe3 (32) or CH2CMe3 (33) (Figure 5)). Compound 33 was also generated by treating 32 with 2.1 equivalents of neopentyl lithium with concurrent elimination of LiCH2SiMe3. 32 shows a fluxional molecule at 25° C by 1H NMR spectroscopy, with the neosilyl groups interchanging between axial and in-plane positions. However, data collection at -60° C shows a static molecule with two broad signals at 178.2 and -222.3 ppm (toluene-d5) for the methylene protons, indicating a C4 symmetry molecule, which is confirmed crystallographically. The U-C distances range from 2.368(7) - 2.418(7) Å; 33 shows analogous distances. The 1H NMR spectrum for 33 has very broad resonances assignable to the methylene coordinated to uranium at 134.5 and -138.8 ppm at 25° C, which become narrower at -50° C, and shift to 223.3 and -221.5 ppm, respectively. Both complexes were stable for days, but decomposed above 45° C to give unidentified paramagnetic products and SiMe4 or CMe4. Adding 1.3 equivalents of LiCH2SiMe3 to 32 creates the charged pair, (X2A2U(CH2SiMe3)3)(Li(THF))2, characterized by resonances at 314.6, 268.8, and -161.0 in the 1H NMR spectrum (THF-d8) for the methylene protons, which shift to 451.0, 378.0, and -236.9 ppm at -75° C. Isolation of the trimethyl ‘ate’ complex (X2A2UMe3)3(Li(dme)) (34) (Figure 5) was possible by adding 3.3 equivalents of MeLi to (X2A2UCl3)3(K(dme))3 in dme, followed by extraction with toluene to remove KCl and LiCl. The molecular structure of 34 shows one U-C distance (2.377(9) Å) within the range observed for the neutral derivatives, with the others (2.493(8) and 2.506(9) Å) being longer, most likely due to an increase in coordination number and overall anionic charge on the complex. Unlike 32 and 33, no signals were noted in the 1H NMR spectrum for the methyl groups between +400 and -400 ppm (THF-d8) for the THF analogue, (X2A2UMe3)(Li(THF))2.

The popular chelating phosphine, bis(1,2-dimethylphosphino)ethane (dmpe), was first introduced to the field of organouranium chemistry by Andersen in 1981 as a way to stabilize uranium(V) alkyls. To (dmpe)UXCl, addition of 4 equivalents of MeLi at -20° C in diethyl ether proceeded to brown-yellow (dmpe)UXMe3 (35). Analysis by 1H NMR spectroscopy at -70° C in toluene-d8 shows an intense singlet at 10.1 ppm for the equivalent methyl groups, but no such resonance was visible by 13C NMR spectroscopy. Despite its low temperature synthesis, 35 is stable at room temperature. Compound 35 reacts with HCl to regenerate the tetrachloride starting material and methane, or phenol to produce (PhO)2UX(dmpe)2 and toluene. Shores and co-workers recently performed further characterization on 35, establishing an average U-C distance of 2.5134(7) Å by X-ray crystallography and a magnetic moment range of 3.23 to 0.49 μB (300 K – 2 K), respectively. With bulkier alkyls, such as benzyl groups, one dmpe ligand is capable of stabilizing the uranium(IV) centre, as demonstrated by using 4 equivalents of benzyl lithium at -70° C, which generates (dmpe)UX(CH2Ph)4 (36). This was recently crystallographically characterized by our group, and showed a distorted trigonal prismatic uranium centre for the U-C and U-P o-bonds. The U-C distances range from 2.460(9) to 2.523(8) Å, supporting each benzyl group is coordinated in an η1-fashion. Performing 1H NMR spectroscopic analysis at -40° C slows the dynamics of the molecule in solution, giving a spectrum with 12 paramagnetically shifted resonances consistent for a C4 symmetric molecule at this temperature. The magnetic moment at 23° C was reported to be 2.70 μB, lower than that for 35, but still on the order of uranium(IV) compounds. Using a 3:1 ratio of benzyl lithium to methyl lithium in the analogous reaction creates the mixed alkyl product, (dmpe)UX(CH2)(CH2Ph)3 (37). Andersen reports the benzyl methylene groups and methyl group appear as single resonances at 1.65 and -0.05 ppm, respectively. Crystallographic characterization shows U-C methylene distances ranging from 2.46(1) - 2.54(1) Å, while that for the methyl group is shorter at 2.41(1) Å (Figure 6). This trend is rationalized based on resonance stabilization of the benzyl carbamion, which lowers the electron density at the sp3 hybridized carbon. As in the case of 36, the benzyl substituents in 37 have structural parameters consistent with η4-bonding.
3.3 Homoleptic: Initial attempts at the synthesis of homoleptic uranium(IV) alkyls have demonstrated that these species are prone to decomposition at temperatures above 0°C. For instance, Marks and Seyam showed that treating UCl₄ with four equivalents of various alkylcubium reagents (LiR, R = Me, iPr, nBu, tBu, neopentyl, 2-cis-2-butenyl, 2-trans-2-butenyl) in NMR tube experiments at -78°C resulted in the desired salt metathesis. However, upon warming, the UR₄ species decomposed, resulting in organics formed from β-hydride and reductive elimination pathways, along with uranium metal. Subsequent to these studies, Evans and co-workers discovered that when UCl₄ was treated with 4 equivalents of LiR (R = nBu, tBu) followed by stirring for 5–6 days, the desired tetravalent uranium alkyls were not formed but rather a reduced trivalent uranium hydride was proposed.

Generation of isolable homoleptic uranium(IV) alkyls has been achieved by the formation of ‘ate’ complexes. Wilkinson and Sigurdson first reported that treating UCl₄ with excess LiR produced the tetravalent uranate compounds [Li(solvent)₂][UR₄] (solvent = THF, Et₂O; R = Me, C₆H₅, o-, m-, p-PhCH₂NMMe₂, CH₂SiMe₃) and in the presence of TMEDA (TMEDA = N,N,N’,N’-tetramethylethylenediamine), Li₃UR₄•7TMEDA. Both elemental analysis and NMR studies carried out at temperatures below 0°C identified the proposed compounds by their integration values, and it was suggested that these anionic complexes were those initially studied by Marks. More recently, however, additional studies have called the identity of the molecules proposed by Wilkinson into question.

Hayton and co-workers have reported a similar series of well-defined, uranium(IV) homoleptic anions. By adding 4.5 equivalents of LiCH₂SiMe₃ to [Li(THF)]₃[U(O'Bu)₄] and excess LiCl, the uranium(IV) salt, [Li₂(UO'Bu)₂Cl][U(CH₂SiMe₃)₂] (38), was formed in low yields. In this case, the LiO'Bu formed in the reaction is retained rather than removed. Characterization by ¹H NMR spectroscopy showed a singlet at 18.42 ppm (benzene-d₆) assigned to the equivalent methylenes coordinated directly to uranium, similar to those in 35, and these have U-C bond lengths ranging from 2.445(6) to 2.485(6) Å determined crystallographically. These U-C bond distances are on the order of those for the trimethyl uranium anion in 34. Compound 38 is stable in the solid state for several days, more so than the derivatives suggested by Gilman. This inherent stability is attributed to the five bulky neosilyl ligands, which coordinately saturate the uranium centre. However, rapid decomposition was noted in solution, due to the lability of the [Li₂(O'Bu)₂Cl] counterion. In an effort to produce more thermally stable compounds, UCl₄ was treated with 5 equivalents of an alkylcubium (LiR, R = CH₂SiMe₃, CH₂Bu) at -25°C, producing [Li(THF)]₃[U(CH₂SiMe₃)₃] (39) (from THF/ether/DME solution) and [Li(THF)]₃[U(CH₂Bu)₃] (40) (from THF/ether solution) in high yields, respectively. Compound 39 was identified by ¹H NMR spectroscopy, which showed the respective methyl and methylene proton resonances at -2.15 and 17.80 ppm (benzene-d₆/THF-d₈). Similarly, these resonances appear at 2.77 and 26.44 ppm for 40 (Figure 7). The molecular structure of 40 showed U-C distances averaging 2.49(3) Å. Both 39 and 40 are stable in the solid state at room temperature for several days, or indefinitely at -25°C; however, both begin to decompose in THF or benzene solution.

Treatment of UCl₄ with 6 equivalents of MeLi in a solution of ether/tetrahydrofuran/TMEDA generated the U(IV) hexa(alkyl) complex [Li(TMEDA)]₃[U(Me₆)₃] (41), which is only stable below -25°C. The ¹H NMR spectrum (THF-d₈) shows a

![Figure 6](image_url) **Figure 6.** Solid state structure of Andersen’s (dmpe)U(ηCH₂Ph₂)(37).

![Figure 7](image_url) **Figure 7.** Solid state structure of the [U(ηCH₂Bu)₃] anion in Hayton’s [Li(THF)]₃[U(ηCH₂Bu)₃](40) (left) and homoleptic uranium(IV) [Li(TMEDA)]₃[U(Me₆)₃] (41) (centre), as well as Bart’s neutral homoleptic uranium(IV) tetra(alkyl), U(ηCH₂Ph₂)₄ (43) (right).
resonance at -19.92 ppm for the equivalent methyl groups, significantly shifted upfield from the 5-coordinate analogue, indicating lithium ion solvation or rapid equilibration at this temperature. Despite its thermal instability, diffraction of single crystals showed an octahedral uranium ion with two Li cations in the secondary coordination sphere. The U-C distances for methyl groups not bonded to Li cations are 2.481(1) and 2.483(9) Å, comparable to 40 (Figure 7). Those coordinated by Li in 41 are lengthened, with U-C distances ranging from 2.55(1) to 2.600(9) Å. Six equivalents of benzylpotassium, when added to a THF solution of UCl4, generated [K(THF)3][K(THF)2][U(CH2CH2CH2)3]2, (42) as a dark red solid in moderate yields. Compound 42 is stable at room temperature for up to one day, or like its other alkyl family members, at -25°C indefinitely, presumably due to ionic pair stabilization and steric saturation of the uranium centre. A resonance for the methylene protons is visible at -25.88 ppm (benzene-d6/THF) in the 1H NMR spectrum, on the order of that for 41 and Cp3UMe2, and the U-C distances range from 2.50(2) to 2.57(2) Å, generating a distorted octahedral uranium ion.

The isolation of neutral homoleptic uranium(IV) species was finally possible by taking advantage of the steric protection imparted by benzyl groups. Tetrabenzylluranium, U(CH2Ph)4 (43), was synthesized by addition of 4 eq. KCH2Ph to UCl4 at -108°C, followed by immediate filtration and workup in diethyl ether to remove KCl. The 1H NMR spectrum (benzene-d6) for 43 showed a resonance at -30.41 ppm for the methylene protons, similar to 42 and Cp3UMe2. The respective p-tolyl and m-xylil derivatives, U(CH2-p-CH2C6H4)2 and U(CH2-m-(CH3)2C6H4)2, were generated in an analogous fashion. With additional electron donation to the benzyl ring by the methyl groups, a successive downfield chemical shift of the methylene resonances is noted, such that the signal for U(CH2-p-CH2C6H4)2 appears at -30.42 ppm and that for U(CH2-m-(CH3)2C6H4)2 is visible at -23.74 ppm. Characterization of 43 by X-ray crystallography shows U-C α-bonds in a pseudotetrahedral arrangement with U-C distances in the range of 2.454(8) - 2.477(7) Å (Figure 7). These neutral tetra(alkyl) species are stable at ambient temperature for one hour, after which time they begin to decompose, mainly by U-C homolytic scission. In contrast to the UR4 derivatives by Marks and Seyam, stability of these species is conferred by the bulky benzyl groups, which coordinate in an η4-fashion. Facile C-C reductive elimination from 43 has been demonstrated using redox-active ligands, which stabilize the uranium(IV) dibenzyl products by storing the two gained electrons in the ligand framework, converting it from a neutral to dianionic chelator while maintaining the tetravalent oxidation state. Both concerted and radical reductive elimination processes are noted, and depend on the reduction potential of the redox-active ligand.

4. Uranium(V) Alkyls

Uranium(V) complexes are exceptionally rare, as disproportionation pathways to generate U(IV) and U(VI) products typically plague this oxidation state. As a result, aside from the pentahalide starting materials, most characterized pentavalent species contain at least one multiple bonded ligand, as these oxidizing ligands help to maintain the +5 oxidation state of the uranium centre. In recent years, advanced experimental and computational techniques have helped highlight the potential role of pentavalent species in Nature and in separations processes. Currently, neutral pentavalent uranium centres with α-bonded hydrocarbyls have eluded isolation and characterization. However, using solvated lithium cations to stabilize the high-valent and coordinatively saturated uranium anions has made study of uranium(V)-carbon bonds possible.

4.1 Homoleptic alkyls: In 1977, Wilkinson and co-workers reported some of the earliest organometallic uranium(V) compounds, a series of homoleptic U(V) octa(alkyls) of the form [Li(dioxane)]2[UR4]. Starting with uranium(V) pentaethoxide in light petroleum, an excess of LiR (R = CH3, CH2SiMe3, CH2CMe3) was added at -70°C and stirred for 1, 16, and 24 hrs, respectively. Upon addition of dioxane to the reaction mixture, the octa(alkyl) uranium complexes precipitate as green solids. Stability of these species decreased as the steric bulk of the alkyl increased, highlighting the role of coordinative saturation of the uranium centre in this family of compounds. These derivatives were identified by elemental analysis and IR spectroscopy, which showed absorptions ranging from 2600-2700 cm⁻¹ for the Li-CH interactions. The 1H NMR spectra all showed downfield shifted broadened resonances for the protons on the α-carbon (pyridine-d5). Treating these species with alcohols protonates the U-C bond, forming the corresponding alkoxy derivatives, and insertion of carbon disulphide into the U-C bonds was noted.

In recent developments, Hayton and co-workers synthesized and definitively characterized an unprecedented homoleptic
uranium(V) hexa(alkyl) ‘ate’ complex. Oxidation of the corresponding U(IV) penta(alkyl) compound, [Li(DME)]_2[U^{IV}(CH_3SiMe_3)_2](39), with 0.5 equiv I_2 in Et_2O at -25 °C, followed by salt metathesis using 1 equiv of Li(CH_3SiMe_3), furnished pentavalent [Li(THF)]_2[U(CH_3SiMe_3)_2](44), after filtration with Et_2O and THF to remove the LiI (eq 7). Compound 44 slowly decomposes above -25 °C, or rapidly in aromatic solvents, by U - C homolytic cleavage. Product identification was possible by ¹H NMR spectroscopy (THF-δ) which showed a resonance at -8.19 ppm for the methylene resonance. The solid state structure of 44 shows an octahedral uranium, with U-C distances of 2.429(8), 2.413(7), and 2.451(6) Å, and a lithium cation surrounded by THF molecules (Figure 8). Interestingly, addition of LiCH_3SiMe_3 to THF solutions of [Li(THF)]_2[U(CH_3SiMe_3)_2] produced no reaction, calling into question the octa(alkyl) complexes originally proposed by Wilkinson. Further characterization by spectroscopic and computational methods shows that 44 behaves similarly to other f′ uranium compounds, with a dominant absorption band at 1462 nm, weak f/f transitions in the near infrared region of the electronic absorption spectrum as well as an anisotropic EPR spectrum. The magnetic moment of 1.54 μB at 300 K, is smaller than the 2.54 μB calculated for the U⁷⁺ ion in a 1F_{5/2} ground state, but comparable to the value for [Li(DME)]_2[U(NCCH_3)_2](1.3 μB). At 4 K, the observed value is 1.19 μB, eliciting a temperature response previously observed for U(V). Computational studies show a substantial uranium f orbital contribution to all of the U-C σ bonds. The three high-energy t_{1u} set of orbitals shows nearly degenerate U-C bonding orbitals that exhibit ~29% 5f-orbital participation. The a_{1g} and e_g orbitals display 13% 7s-orbital and 22% 6d-orbital participation, respectively. No 7p-orbital contribution in the six U-C bonds is noted.

4.2 Alkoxide supported alkyls: Hayton has also demonstrated monodentate alkoxide ligands are effective ancillary ligands to support organouranium(V) species. Addition of 0.5 equiv. Me_3NO to [Li(DME)]_2[U^{IV}(CH_3SiMe_3)_2(OBu)_2] in DME at -25°C produced the uranium(V) alkyl derivative, [Li(DME)]_2[U(CH_3SiMe_3)_2(OBu)_2](45) in moderate yield (43%) (eq 7). Analysis by ¹H NMR spectroscopy (THF-δ) showed a resonance at -0.38 ppm for the equivalent methylene protons, just upfield of the homoletic anion 44. Compound 45 is more thermally stable than its homoletic counterpart, indicating the alkoxyl groups contribute to stabilizing the complex. Due to the complexity of the reaction, some of the uranium(IV) starting material likely acts as a sacrificial oxygen acceptor, accounting for the observed low yield. The octahedral uranium centre in 45 has tert-butoxy groups trans to each other, with the alkyl substituents in the equatorial plane. The equivalent neosilyl groups have a U-C distance of 2.42(2) Å, within error of those for 44. The magnetic moment of 45 is also similar to that for 44, ranging from 1.44 μB at 300 K to 1.05 μB at 4 K.

5. Uranium(VI) Alkyls

Hexavalent uranium compounds are perhaps the best known and most well-studied actinide complexes, due in part to the ubiquity of the uranyl ion, [UO_2]^{2+}, and the utility of volatile UF_6 in isotope separation. Despite the popularity, thermodynamic stability, and operational simplicity of this oxidation state, relatively little is known about the synthesis and stability of uranium(VI)-carbon σ-bonded alkyls.

5.1 Uranyl: Examples of hexavalent alkyls were first reported in 1982 by Seyam, who created a family of dialkyl dioxoranium(VI) complexes. Starting from UO_2Cl_2 in either toluene or THF, 2 equivalents of LiR or MgClR’ (R = CH_3, t-C_3H_7, C_6H_5; R’ = CH_2CH_2C_3H_7, C_6H_5) were added at -78°C (eq. 8). These compounds are thermally unstable, decomposing at ambient temperature to afford “UO,” and organics. Alkanes, alkenes, and coupled products were observed, depending on the alkyl group. Homolytic scission, β-hydride elimination, and in the case of phenyl, C-C reductive elimination were operative U-C decomposition pathways.

Expanding on this work, Hayton and co-workers have generated a coordinatively saturated uranium(VI) alkyl ‘ate’ complex. Treating a -25°C THF solution of UO_2Cl_2 with 4 equivalents of Li(CH_3SiMe_3) in DME results in formation of green [Li(DME)]_2[UO_2(CH_3SiMe_3)_2] (46), which is thermally sensitive and decomposes at room temperature in a few hours (eq. 8). Thus, ¹H NMR spectroscopic data were acquired at -1.6°C (THF-d_8), and showed a resonance at -3.80 ppm corresponding to the equivalent methylene groups, upfield of the uranium(V) compounds. Additionally, the resonance for the methylene carbon was also found by ¹³C NMR spectroscopy at 242.9 ppm, and supports the presence of Li-O(uranyl) interactions in solution. The U-C bond distances of 2.497(6) and 2.481(6) Å are slightly longer as compared to those calculated for [U(CH_3SiMe_3)_2] (vide infra) and may be due in
part to U-C antibonding character in the U-O σ-bonding molecular orbital. The stability of 46 highlights that Li coordination serves to stabilize the tetraalkyl species in contrast to the original uranyl derivatives reported by Seyam.

Eqn. 8 Synthesis of uranium(VI) alkyls, [Li(DME)]_2[UO_2(CH_2SiMe_3)_3] (46) (left) and UO_2R_2 (right).

5.2 Oxo alkyls: Recently, Schelter and co-workers have synthesized a stable U(VI) mono-oxo methyl compound, which is the first example of a uranium(VI) methyl species. Starting from U^{IV}Me(N(SiMe_3)_2), in diethyl ether at -21°C, N-methylmorpholine-N-oxide is used as an oxidant to form dark red U^{V}(O)Me(N(SiMe_3)_2). Interestingly, solutions of U^{VI}(O)Me(N(SiMe_3)_2) are stable over several days at room temperature, which is in sharp contrast to the other uranium(VI) alkyls reported here. Characterization by multinuclear NMR spectroscopy shows a resonance for the methyl coordinated to uranium at -2.57 ppm in the ^1H spectrum and at 301.0 ppm in the ^13C spectrum (benzene-d_6), both of which are consistent with 46. X-ray crystallography establishes the U-C distance of 2.343(4) Å, which is the shortest known terminal alkyl U-C bond. This is due in part to the small radius of U(VI), as well as the inverse trans influence, which causes mixing of the trans U-O and U-C σ-bonds, serving to strengthen the U-C bond and impart thermal stability.

5.3 Homoleptic alkyls: The only homoleptic uranium(VI) alkyl, which happens to be neutral, was recently reported by Hayton and co-workers. Formation of a stable hexavalent species was predicted by electrochemical oxidation of [Li(THF)]_2[U^{IV}(CH_2SiMe_3)_3]. Addition of U(OBu)_{6+} a mild chemical oxidant, to [Li(DME)]_2[U^{IV}(CH_2SiMe_3)_3] in THF at -25°C forms neutral deep gold U^{IV}(CH_2SiMe_3)_3 (47) and [Li(THF)]_2[U(OBu)_{6+}]. Thus, assignment of 47 is supported by resonances in the ^1H NMR spectrum (THF-d_6, -40°C) at -3.15 and 0.52 ppm in a 2:9 ratio for the methyl and methylene resonances, respectively, and by resonances at 434.3 and 11.12 ppm, for the methylene and methyl carbons of the neosilyl ligand in the ^13C(^1H) NMR spectrum (THF-d_6, -46°C), respectively. Although 46, 47, and U^{IV}(O)Me(N(SiMe_3)_2) are diaimagnetic, the extreme chemical shifts of their protons are attributed to relativistic spin–orbit (SO) coupling.

Compound 47 is only observable at low temperatures (-40° - -25°C), thus computational methods were used to deduce its structure. The alkyl substituents were calculated to have U-C bond distances ranging from 2.353 to 2.377 Å with an octahedral geometry about the uranium centre. Slightly higher than the pentavalent analogue, the t_{1u} set of orbitals shows ~35% 5f-orbital participation while the a_{1g} and e_g set exhibits 10% 7s-orbital participation and 18% 6d-orbital participation, respectively. The authors note that f-orbital participation increases with oxidation state of the uranium centres, while 7s and 6d participation keeps constant. The uranium component of the U-C bonds is significant, indicating strong covalent interactions. Despite the low thermal stability, formation of 47 is a significant advance in high-valent uranium-carbon bonds and highlights strong metal-ligand covalent interactions for an actinide.

6. Metallacyclic Alkyls

Metallacyclic alkyl groups, where the alkyl is bonded to the uranium centre in a ring, are often notable because of their interesting spectroscopic and crystallographic properties. Common routes to their formation can be either 1) by cyclometallation via intramolecular C-H activation by a coordinatively unsaturated, highly reactive uranium centre, or 2) by introduction of alkyl groups in ancillary ligand frameworks, which generate metallacycles upon coordination.

6.1 Cyclometalation of Silyl Substituents: Sattelberger and co-workers observed an early example of a cyclometallated uranium(IV) alkyl, Cp^2+U(CH_2SiMe_3)PSiMe_3 (48), by C-H activation of SiMe_3 in Cp^2+U(CH_3)P(SiMe_3)_2 upon heating to 120°C in benzene (Figure 9). Concurrent with its formation is release of methane. Crystallographic determination confirmed the presence of the metallacycle, with a uranium-carbon bond distance of 2.415(20) Å. This distance is similar to those for non-cyclometallated uranium(IV) alkyl species. A single resonance for the protons on the methylene carbon coordinated directly to uranium appears at -201.60 ppm in the ^1H NMR spectrum, upfield of that of Cp^2UMe_3.

Figure 9. Cyclometallated uranium alkyls species, 49 (left), 55 (centre), and 58 (right).

Trimethylsilyl C-H activation was also noted by Andersen and co-workers, who synthesized tetravalent [(Me_3Si)_2N]_2U(CH_2SiMe_2NSiMe_3) (49), a cyclometallated uranium alkyl amide from multiple reaction pathways (Eq. 9). Heating [(Me_3Si)_2N]_2UMe to 140°C for 45 minutes followed by increasing the temperature of the melt to 150-160°C for an additional 10 minutes produced the desired complex plus methane, as did treating [(Me_3Si)_2N]_2UCl in pentane at 0°C with an equivalent of LiEt in toluene (0.47 M), followed by stirring at 0°C for 16 hours. This forms “[(Me_3Si)_2N]_2UEt”, which avoids β-hydrogen elimination by cyclometallating to form 49 and ethane. Compound 49 can also be formed through
pyrolysis of solid [(Me2Si)2N]UCl at 200 °C with extrusion of dihydrogen. While crystallographic data were not obtainable, positive identification was gained from combustion analysis, mass spectrometry, and 1H NMR spectroscopy, which showed a resonance at -128.6 ppm (benzene-d6) for the methylene protons adjacent to uranium, downfield of those for 48. Formation of 49 is significant as it is an important intermediate in hydrogen/deuterium exchange by uranium(IV) trimethylsilylamide species.

Compound 49 has proven to be a useful synthon for metallacyclic derivatives. Recently, Ephritikhine and co-workers created a series of bis(metallacyclic) U(IV) complexes, [ML2]{{U[N(SiMe3)2](CH2SiMe2NSiMe3)}2} (M = Li (50), Na (51), K (52); L = THF or crown ethers) (eq. 9). Treating [(Me3Si)2N]UCl2SiMe3 (49) with LiCH2SiMe3 at 140 °C, 45 min; 2)160 °C, 10 min produced a negligible chemical shift of the protons of the methylenes coordinated to uranium at 286.20 and 43.10 ppm. The corresponding U-C distances in 53 are 2.362(19), 2.284(19), and 2.415(6) Å; those for 54 are 2.361(4), 2.352(5), and 2.339(4) Å, shorter than the U-C distance in 49.

A rare example of cyclometallation by deprotonation of bis(trimethylsilyl)amide ligands has been reported to afford uranium trimers, as demonstrated by Gambarotta and co-workers. Addition of LiCH2SiMe3 to UCl3/N(SiMe3)2]2(DME) in hexane at ambient temperature produced the trinuclear cluster, U[μ-(CH2SiMe3)N(SiMe3)]2U[N(SiMe3)2]2:U[μ(C-C-SiMe3)N(SiMe3)]2U[μ-(OMe)] (53), where each uranium centre is tetravalent (Figure 10). Removing the solvent from the starting material produced a similar trinuclear uranium cluster without the bridging OMe, U[μ-(CH2SiMe3)N(SiMe3)]2U[N(SiMe3)2]2:U[μ(C-C-SiMe3)N(SiMe3)]2U[μ-(OMe)] (54) (Figure 12). In 53, the protons for the bridging methylene units appear at -46.90 ppm in the 1H NMR spectrum, whereas for 54 they are found at -43.10 ppm. The corresponding U-C distances in 53 are 2.362(19), 2.284(19), and 2.415(6) Å; those for 54 are 2.361(4), 2.352(5), and 2.339(4) Å, shorter than the U-C distance in 49.

Cyclometallated clusters via C-H activation of silyl groups were also observed by Hayton and co-workers, who reported that adding half an equivalent of NaN3 to U(N(SiMe3)2]2 created a dinuclear U(IV) cyclometallated bridging nitrido, [Na(DME)2(TMEDA)]{N(SiMe3)2}2U(μ-N)(CH2SiMe3N-SiMe3)U[N(SiMe3)2]2 (55) (Figure 9). U-C distances were found to be 2.51(1) and 2.88(1) Å, but the protons on the methylene were not observed by 1H NMR spectroscopy. Oxidation of 55 with half an equivalent of I2 created the mixed-valent U(IV/V) nitrido dimer, (N(SiMe3)2)2U(μ-N)(CH2SiMe3N(SiMe3)2U(N(SiMe3)2)2 (56) by elimination of...
On conversion, the methylene carbon is no longer bridging, giving rise to one U-C distance of 2.427(8) Å. The protons on the α-carbon are visible at -76.74 ppm in the $^1$H NMR spectrum. Oxidation of 55 with 1 equivalent of trimethyamine-N-oxide generates the mixed U(V/IV) oxo species, $[^{\text{Na(DME)}_2}]_2[^{(\text{N(SiMe}_3)_2)}_2(\text{O})_{\mu-N}]_{\text{U}(\text{CH}_3\text{SiMe}_3\text{N})_{\eta-\text{cyclohexane}}_{\eta-\text{SiMe}_3}]_{\text{U}(\text{N(SiMe}_3)_2)}_2$ (57) (left), Liddle’s “tuck-in-tuck-over-tuck-over”, $[^{\text{Na(DME)}_2}]_2[^{(\text{N(SiMe}_3)_2)}_2(\text{O})_{\mu-N}]_{\text{U}(\text{CH}_3\text{SiMe}_3\text{N})_{\eta-\text{cyclohexane}}_{\eta-\text{SiMe}_3}]_{\text{U}(\text{N(SiMe}_3)_2)}_2$ (58) (right) and Evans’s “tuck in” $[^{(\text{N(SiMe}_3)_2)}_2(\text{O})_{\mu-N}]_{\text{U}(\text{CH}_3\text{SiMe}_3\text{N})_{\eta-\text{cyclohexane}}_{\eta-\text{SiMe}_3}]_{\text{U}(\text{N(SiMe}_3)_2)}_2$ (59) (centre), and Evans’s “tuck in” $[^{(\text{N(SiMe}_3)_2)}_2(\text{O})_{\mu-N}]_{\text{U}(\text{CH}_3\text{SiMe}_3\text{N})_{\eta-\text{cyclohexane}}_{\eta-\text{SiMe}_3}]_{\text{U}(\text{N(SiMe}_3)_2)}_2$ (60) (right). The resonance for the methine proton appears at 3.84 ppm, while that for the “tuck-over” to generate new uranium species, $[^{(\text{N(SiMe}_3)_2)}_2(\text{O})_{\mu-N}]_{\text{U}(\text{CH}_3\text{SiMe}_3\text{N})_{\eta-\text{cyclohexane}}_{\eta-\text{SiMe}_3}]_{\text{U}(\text{N(SiMe}_3)_2)}_2$ (60) (right). The resonance for the methine proton appears at 3.84 ppm, while that for the “tuck-over” to generate new uranium species, $[^{(\text{N(SiMe}_3)_2)}_2(\text{O})_{\mu-N}]_{\text{U}(\text{CH}_3\text{SiMe}_3\text{N})_{\eta-\text{cyclohexane}}_{\eta-\text{SiMe}_3}]_{\text{U}(\text{N(SiMe}_3)_2)}_2$ (60) (right). The resonance for the methine proton appears at 3.84 ppm, while that for the “tuck-over” to generate new uranium species, $[^{(\text{N(SiMe}_3)_2)}_2(\text{O})_{\mu-N}]_{\text{U}(\text{CH}_3\text{SiMe}_3\text{N})_{\eta-\text{cyclohexane}}_{\eta-\text{SiMe}_3}]_{\text{U}(\text{N(SiMe}_3)_2)}_2$ (60) (right). The resonance for the methine proton appears at 3.84 ppm, while that for the “tuck-over” to generate new uranium species, $[^{(\text{N(SiMe}_3)_2)}_2(\text{O})_{\mu-N}]_{\text{U}(\text{CH}_3\text{SiMe}_3\text{N})_{\eta-\text{cyclohexane}}_{\eta-\text{SiMe}_3}]_{\text{U}(\text{N(SiMe}_3)_2)}_2$ (60) (right). The resonance for the methine proton appears at 3.84 ppm, while that for the “tuck-over” to generate new uranium species, $[^{(\text{N(SiMe}_3)_2)}_2(\text{O})_{\mu-N}]_{\text{U}(\text{CH}_3\text{SiMe}_3\text{N})_{\eta-\text{cyclohexane}}_{\eta-\text{SiMe}_3}]_{\text{U}(\text{N(SiMe}_3)_2)}_2$ (60) (right).
but are on the order of those in 59. Resonances for either set of methylene protons could not be clearly assigned by $^1$H NMR spectroscopy. Additional C-H reductive elimination occurs with the newly formed alkyl hydride, 61, in the presence of PhSSPh, PhN=NPPh, and cyclooctatetraene. Protonation of the uranium alkyl in 61 occurs upon addition of D$_2$, PhSH, and PhNH$_2$. Similarly, heating (CP$_8^{66\text{Me}}$)$_2$UMe$_2$ in toluene at 110°C for 4 hours led to cyclometallation of the SiMe$_3$ group of both ligands with concomitant loss of 2 equivalents of methane, forming [(η$^3$-C$_5$Me$_5$EtSiMe$_2$CH$_2$)$_2$U] (62).$^{37}$ The molecular structure shows a U-C distance of 2.453(2) Å for the new “tucked-in” methylene groups (Figure 11), and these protons were not visible by $^1$H NMR spectroscopy. Compound 62 undergoes further chemistry of the uranium-alkyl bond, readily inserting CO, $^3$PrN=C=N$^3$Pr, CS$_2$, and N$_3$Ad, or facile protonation with pyridine-N-oxide. Heating complexes of the form Cp$^6$(C$_9$H$_8$)UR (R = Me, Ph) generates (η$^3$-C$_5$H$_5$)(η$^3$-C$_5$Me$_5$EtSiMe$_2$CH$_2$)U (63) with loss of RH.$^{98}$ The resonance for the methylene appears at -67.4 ppm in the $^1$H NMR spectrum for 63. Single crystals were isolated as the THF adduct, (η$^3$-C$_5$H$_5$)(η$^3$-C$_5$Me$_5$EtSiMe$_2$CH$_2$)U(THF) (64), and analysis showed two crystallographically independent molecules in the unit cell. The U-C distances of 2.586(7) and 2.596(6) Å are longer than typical for non-cyclometallated uranium(IV) species, but are on the order of those observed for 61. The U-C α-bond in 63 readily undergoes 1,2-insertion of isonitriles, generating the iminoaryl uranium product.

$$\text{Eq. 10. Formation of 61 via reductive elimination of dihydrogen.}$$

**63 Uranium Methanide Complexes:** The first uranyl methanide compound, which features the U-C alkyl bond in a 6-membered metallacycle, was reported by Sarsfield in 2002.$^{39}$ Synthesis was accomplished by addition of one equivalent of [Na(CH$_2$PPh$_3$SiMe$_2$)$_2$]$_2$ to UO$_2$Cl$_2$(THF)$_3$, which afforded a deep red dimeric product, [UO$_2$(CH$_2$PPh$_3$SiMe$_2$)$_2$](THF)$_3$, in good yield (eq. 11). The methine proton is observable at 2.52 ppm (CD$_2$Cl$_2$) in the $^1$H NMR spectrum, which is significantly downfield compared to those observed for 46 and 47. The equivalent uranium centres have a distorted pentagonal bipyramidal geometry, with a U-C distance of 2.691(8) Å, suggestive of a U(VI)-C bond as it is smaller than the Van der Waals radii (3.56 Å) and on the order for the U-N bonds (2.514(7), 2.458(7) Å). Characterization and crystallization in THF produces the monomeric species, UO$_2$Cl(CH$_2$PPh$_3$SiMe$_2$)$_2$(THF) (65), which shows the methine proton at 2.28 ppm in thf-$d_8$, a carbon resonance at 19.5 ppm in the $^1$C NMR spectrum, and a U-C distance of 2.707(4) Å in the range of that for the dimer (eq 11). Liddle has recently reported that treating 65 with one-half equivalent of sodium benzyll in THF results in reduction, producing the mixed valent uranium(V,VI) dimer, [UO$_2$(CH$_2$PPh$_3$SiMe$_2$)$_2$][Cl$^-$](μ-Cl)UO$_2$(μ-O)(CH$_2$PPh$_3$SiMe$_2$)$_2$], along with 0.25 equivalents of benzil.$^{100}$ The formation of this dimeric species is significant as it is a rare example of an organometallic uranyl(V) species. The mixed valency creates a $^1$H NMR spectrum with both sharp diamagnetic and broad paramagnetic resonances, showing C-H protons appearing at 3.40 and -4.14 ppm, respectively (benzene-δ$_2$). Respective distances of 2.732(6) and 2.735(6) Å for the uranium(VI) and uranium(V) centers are indistinguishable based on error values.

$$\text{Eq. 11. Monomer-dimer equilibrium for uranium methanide complex 65.}$$

Ephrithikhine has accomplished synthesis of mono- and bis(methanide) species, by treating [UO$_2$(OTf)$_2$]$_2$ with either one or two equivalents of LiHC(Ph$_2$PS)$_2$ in diethyl ether, respectively.$^{101}$ The mono(ligand) derivative, [UO$_2$(CH$_2$Ph$_2$PS)$_2$(OTf)(OEt$_2$O)] (66), and bis(ligand) compound, [UO$_2$(CH$_2$Ph$_2$PS)$_2$]$_2$(THF) (67), were both isolated as red solids. The molecular structure of 66 shows a pentagonal bipyramidal uranium centre, with a U-C distance of 2.647(12) Å. This distance is smaller than those seen for 65 and its dimeric counterpart. Complex 67 is the first bis(methanide) uranyl complex to be generated, and shows a resonance at 2.60 ppm (THF-$d_8$) at room temperature for equivalent methine protons, very close to that observed for 65. However, cooling of the sample to -107°C results in decoalescence of the signal, indicating a dynamic process in solution. One of the methanide ligands is almost planar, and displays a U-C bond of 2.656(3) Å, while the other ligand shows a boat conformation, with a long U-C distance of 3.863(3) Å. The long distance in the latter case indicates no U-C bond, thus 67 can more correctly be thought of as a zwitterion, with a cationic uranium and an anionic carbon. Thus, the dynamic process noted by $^1$H NMR spectroscopy is interchange between the bi- and tridentate ligand.

**7. Conclusions and Outlook**

The works highlighted in the previous pages demonstrate representative, significant advances in the synthesis, isolation, and characterization of uranium-alkyl compounds. From initial experiments that gave rise to the notion that uranium-carbon bonds are inherently unstable has blossomed a useful, albeit unpredictable, field that takes advantage of the potential covalency of uranium. It is clear from the results presented herein that there is no general synthetic route to building uranium alkyls, as small variations in ligands, reagents, leaving groups and solvents dictate formation and isolation of the desired U-C bonds. Additional complexities exist when there is no steric protection by omission of ancillary ligand frameworks altogether. However, despite the important advances described
within, several frontiers and opportunities still exist for uranium alkyl species. Synthesis of families of neutral uranium(V) and uranium(VI) complexes, with or without ancillary ligands, has not yet been accomplished. Uranium alkyl derivatives supported by chiral ligand frameworks have not yet been realized either, but would provide an opportunity for selective transformations.

In the examples discussed herein, these U-C α-bonds have proven to be quite reactive towards small molecules, readily undergoing insertion and protonation in analogy to their transition metal counterparts. Relative to the d-block, however, the reactivity of organouranium species is still underexplored, especially when considering fundamental organometallic transformations. For instance, utilizing intermolecular oxidative addition as an easy and predictable synthetic route to uranium-carbon bonds still remains to be demonstrated, as does general reductive elimination for C-C and C-H bond formation, an important step in substrate release from uranium centres. α-Hydride abstraction of uranium alkyls has not yet been demonstrated, and would provide a route to the synthesis of uranium alkylidene species. Further, understanding when β-hydrogen elimination occurs for uranium alkyls would be an important advance. Facilitating or blocking this reaction in desired cases would open a door for generation of uranium hydrides and uranium based catalysts. Migratory insertion of non-polar substrates, such as olefins, has been demonstrated on large scales in uranium-mediated polymerization, but not for the synthesis of small molecules. With the ultimate goal of elevating the understanding of organouranium species to be equal to that of their transition metal counterparts, further development of uranium alkyl chemistry is needed.

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Notes and references
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53. Measured by SQUID magnetometry.


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This Perspective highlights the synthesis, characterization, and reactivity of significant organouranium complexes with σ-bonded alkyl ligands.