# 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

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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.[1] [2] Compounds containing uranium-carbon σ-bonds were especially desirable, as these ligands conferred such volatility to transition metal derivatives,[3, 4] 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.[5] 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."[1] 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.[1]

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, $Cp_3UR$,[6, 7] did the opinion of uranium alkyl species begin to change. The stability of the $Cp_3UR$ 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 metallocene 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 "$UR_4$" compounds quickly decomposed during warming,[8] 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 $[Li(solvent)]_2[UR_6]$ that uranium alkyls were isolated in the absence of ancillary ligands.[9]

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 alkyllithium 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 σ-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 σ-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 homoleptic 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 $UI_3(THF)_4$[10] and its recent relative, $UI_3(dioxane)_{1.5}$,[11] 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 σ-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, $Cp^*_2UCH(SiMe_3)_2$ (**1**). Marks and co-workers discovered that treating the uranium(III) chloride trimer, $[Cp^*_2U(\mu\text{-}Cl)]_3$, with $LiCH(SiMe_3)_2$ in diethyl ether at room temperature afforded the desired product with loss of LiCl (Figure 1).[12] 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 $Cp^*_2UCH(SiMe_3)_2$ as a monomer. Hydrogenation of $Cp^*_2UCH(SiMe_3)_2$ results in formation of the trivalent monohydride dimer, $[Cp^*_2UH]_2$. Similarly, Evans and co-workers showed successful alkylation of the sterically crowded $[Cp^*_2U]_2(\mu\text{-}\eta^6{:}\eta^6\text{-}C_6H_6)$ 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, $[Cp^*(CH(SiMe_3)_2)U]_2(\mu\text{-}\eta^6{:}\eta^6\text{-}C_6H_6)$ (**2**) (Figure 1).[13] A resonance assignable to the methine proton was not visible in the $^1H$ NMR spectrum, but crystallographic data confirmed the structure, with a $U\text{-}C_{alkyl}$ distance of 2.508(2) Å.

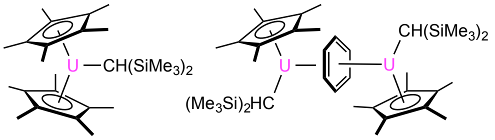

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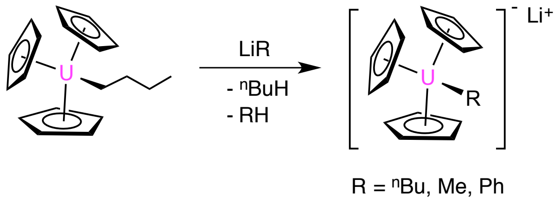
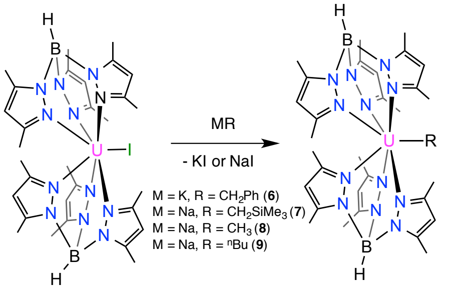
**Figure 1.** Uranium(III) alkyls derived from $LiCH(SiMe_3)_2$: $Cp^*_2UCH(SiMe_3)_2$ (**1**) and $[Cp^*(CH(SiMe_3)_2)U]_2(\mu\text{-}\eta^6{:}\eta^6\text{-}C_6H_6)$ (**2**).

In 1986, Folcher and co-workers reported that $Cp_3U^nBu$ could be reduced to a family of uranium(III) alkyl anions, $[Cp_3UR]^-$, by treatment with one equivalent of LiR (R= $^n$Bu (**3**), Me (**4**), Ph (**5**)) (eq. 1).[14] 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 $Cp_3U^nBu$ in diethyl ether/benzene, therefore benzene loss could not be detected. $^1H$ NMR spectroscopic data (benzene-$d_6$)[15] showed the formation of the uranium(III) alkyl anion in each case, with resonances visible for the $^n$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 $[Cp_3U^nBu][Li]$ and $C_{14}H_{28}N_2O_4$ (2.1.1 cryptand) through scintered 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(l)° (Figure 2). The neutral uranium(IV) starting material, $Cp_3U^nBu$,[16] has a shorter $U\text{-}C_{nBu}$ 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).[17]



**Eq. 1.** Synthesis of Folcher's uranium(III) alkyl anion family.

**2.2 Tp* Derivatives:** Analogous to cyclopentadienyl ligands are hydrotris(1-pyrazolyl)borates (Tp), which were first reported on uranium by Bagnall and co-workers in 1974.[18] Since then, the bulkier methylated derivative, hydrotris(3,5-dimethylpyrazolyl)borate (Tp*), has been used to stabilize uranium(III) centres. Generation of $Tp^*_2UI$[19] and $Tp^*UI_2$[20, 21] from $UI_3(THF)_4$ and KTp* have made using alkyl substituents



**Eq. 2.** Synthesis of $Tp^*_2UR$ complexes (**6-9**).

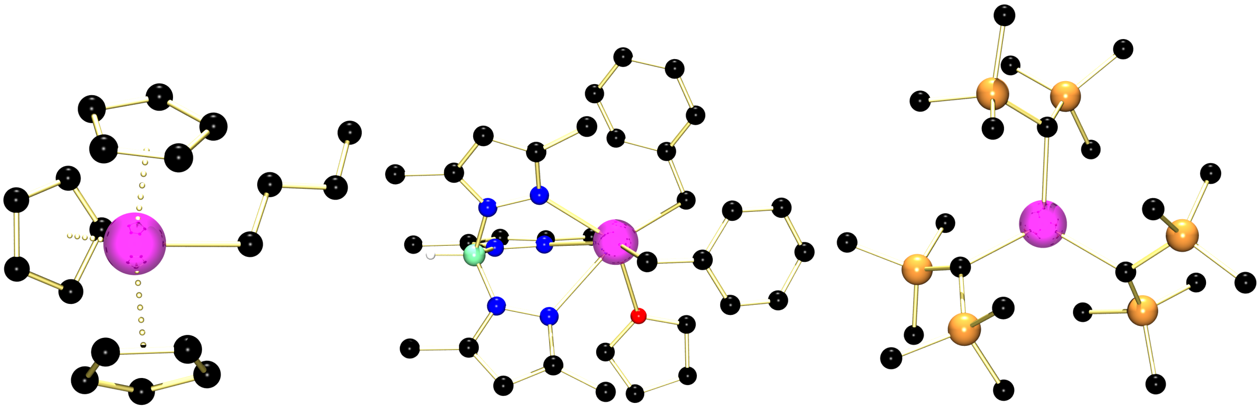
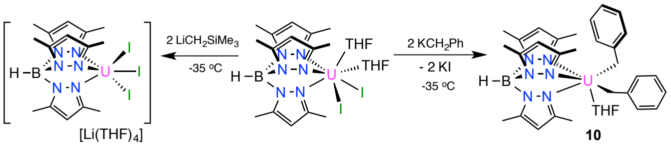


**Figure 2.** Solid state structures of uranium(III) alkyls: Folcher's $[Cp_3U^nBu]^-$ (**3**) (left), Bart's $Tp^*U(CH_2Ph)_2(THF)$ (**10**) (centre), Sattelberger's $U(CH(SiMe_3)_2)_3$ (**11**) (right). The lithium counter ion in **3** has been removed for clarity.

smaller than $–CH(SiMe_3)_2$ on uranium possible. Recently, a family of trivalent alkyls of the form $Tp^*_2UR$ (R = $CH_2Ph$ (**6**), $CH_2SiMe_3$ (**7**), $CH_3$ (**8**), $^nBu$ (**9**)) was synthesized via salt metathesis with $KCH_2Ph$, $NaCH_2SiMe_3$, NaMe or $Na^nBu$ in THF at -35° (eq. 2), respectively, eliminating KI or NaI.[22, 23] Grignard reagents were unsuccessful in the formation of **6-9**, instead producing the halide exchange product. Characterization by $^1H$ NMR spectroscopy (benzene-$d_6$) 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 $^1H$ NMR data collected at -15° C (toluene-$d_8$) 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 ($CH_3$), 2.57(2) Å ($CH_2Ph$), and 2.601(9) Å ($CH_2SiMe_3$) that are on the order of those in **4** and track with increasing sterics of the alkyl group. A magnetic moment (23° C) of 2.6 $\mu_B$ was measured for compounds **7** and **8**, while that of **6** was found to be 2.5 $\mu_B$.[24] Compound **6** readily undergoes insertion of $CO_2$ or $CS_2$ to generate the respective uranium(III) carboxylate, $Tp^*_2U(\kappa^2\text{-}O_2CCH_2Ph)$, and thiocarboxylate, $Tp^*_2U(\kappa^2\text{-}S_2CCH_2Ph)$.[23] The U-C σ-bond in **6** is easily protonated with terminal alkynes, amines, and thiols to generate the corresponding uranium(III) family, $Tp^*_2UX$ (X = CCPh, $CCSiMe_3$, NHPh, $NHCH_2Ph$, SPh).[25] In the presence of organoazides or diazoalkanes, **6** reacts to form the oxidized uranium(IV) imido complexes, $Tp^*_2UNR$ (R = Mes, Ph, Ad),[26] or hydrazonido complexes, $Tp^*_2U(\eta^2\text{-}N_2CPh_2)$ and $Tp^*_2U(\eta^1\text{-}N_2CHSiMe_3)$,[27] with loss of benzyl radical that subsequently couples and is identified as bibenzyl.

The Tp* ligand also supports the uranium(III) dialkyl, $Tp^*U(CH_2Ph)_2(THF)$ (**10**),[28] whose synthesis is achieved by addition of $KCH_2Ph$ to $Tp^*UI_2(THF)_2$ in THF at -35° C, with loss of KI (eq 3). Identification by $^1H$ NMR spectroscopy (THF-$d_8$) showed a resonance for the equivalent methylene protons at 0.04 ppm. The U-C σ 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 $\eta^4$-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 $Tp^*U(CH_2SiMe_3)_2$ with $LiCH_2SiMe_3$ under the same conditions resulted in isolation of $[Li(THF)_4][Tp^*UI_3]$, presumably due to side reactions with eliminated LiI that is soluble in THF (eq. 3).[22] As is the case for **6**, mesityl azide oxidizes **10,** forming the uranium(IV) alkyl imido species, $Tp^*U(NMes)CH_2Ph$, and half and equivalent bibenzyl, again indicating benzyl radical extrusion.



**Eq. 3.** Salt metathesis reactions of $Tp^*UI_2(THF)_2$ (**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 $U(O\text{-}2,6\text{-}^tBu_2Ph)_3$ with three equivalents of $LiCH(SiMe_3)_2$ in hexanes at room temperature for 2 hours afforded $U(CH(SiMe_3)_2)_3$ (**11**).[29] The eliminated lithium aryloxide, $LiO\text{-}2,6\text{-}^tBu_2Ph$, is soluble in hexane, facilitating separation from the desired organouranium species by repeated washing. As in the case for $[Cp^*(CH(SiMe_3)_2)U]_2(\mu\text{-}\eta^6{:}\eta^6\text{-}C_6H_6)$, the $^1H$ NMR spectrum (benzene-$d_6$) 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 $U(CH_3)_3$, and found to be due to the contribution of the uranium 6d orbitals, rather than 5f orbitals, in the uranium-carbon bonds.[30] 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 γ-hydrogen abstraction. Magnetic studies from 100 – 270 K revealed a $\mu_{eff} = 3.0\ \mu_B$, comparable to that observed in $U(N(SiMe_3)_2)_3$,[31] and higher than those for **6-8**. Addition of HO-2,6-$^tBu_2Ph$ to **11** regenerated the uranium tris(aryloxide) starting material. Traditional reaction pathways through salt metathesis using $UCl_3(THF)_x$ and $LiCH(SiMe_3)_2$ did not give the desired product, but similarly to the chemistry with Tp*, produced the lithium 'ate' complex, $[Li(THF)_3][UCl(CH(SiMe_3)_2)_3]$ from reaction of the alkyl species with LiCl.

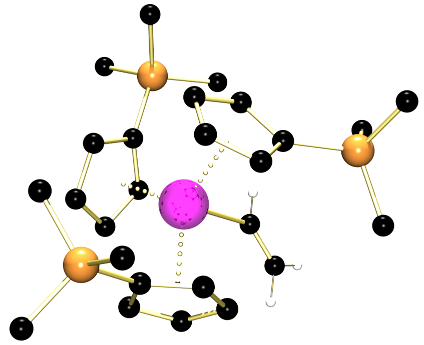


**Figure 3.** Solid state structure of Marks' uranium(IV) vinyl species, $Cp'_3UCHCH_2$.

## 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 $Cp_3UCl$ in diethyl ether with three equivalents of LiR (R = Me (**12**), $^nBu$, allyl (**13**), neopentyl (**14**), $C_6F_5$, $^iPr$)[7] or MgXR ($R{=}CH_3C(CH_2)_2$,[32] $^tBu$,[7] *cis*-2-butenyl,[7] *trans*-2-butenyl,[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. $^1H$ NMR spectroscopic measurements (benzene-$d_6$) confirmed product formation. Compared to uranium(III) alkyls, the chemical shifts reported for protons on the α-carbon of uranium(IV) alkyls appear downfield. For example, resonances for the protons on $sp^3$-hybridized α-carbons range from 186 (**14**) to 202 ppm (**12**), while that for the proton on the $sp^2$ α-carbon in **15** appears at 163.3 ppm. The allyl ligand in **13** undergoes a σ/π conversion on the NMR timescale, causing a shift in the single resonance for the equivalent α-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 $Cp^*_2UMe_2$ (**16**), the first member of the uranium(IV) dialkyl family, produced by addition of 2 equivalents of MeLi to a diethyl ether suspension of $Cp^*_2UCl_2$ at -78° C, followed by filtration to remove LiCl and recrystallization in toluene (eq. 4).[33] As an organoactinide 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 $^1H$ 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 (*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 σ bonds of 2.424(7) and 2.414(7) Å, and a C-U-C angle of 94.5(3)°.[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 $Cp^*_2UMe_2$, additional members of the dialkyl family, $Cp^*_2U(CH_2SiMe_3)_2$,[37] $Cp^*_2U(CH_2Ph)_2$,[38] $Cp^*_2UPh_2$,[37] were soon synthesized by similar procedures. The monoalkyl variants, $Cp^*_2URCl$, 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 $Cp''_2UMe_2$ ($Cp'' = \eta^5$-1,3-$(SiMe_3)_2C_5H_3$)[40], $Cp^‡_2UMe_2$ ($Cp^‡ = \eta^5$-1,3-$(CMe_3)_2C_5H_3$),[40] and $(Cp^{tBu3})_2UMe_2$ ($Cp^{tBu3} = \eta^5$-1,2,4-$(Me_3C)_3C_5H_2$) using the same experimental conditions. Evans and co-workers synthesized $Cp^{Me4}{}_2UMe_2$ ($Cp^{Me4} = \eta^5$-$C_5Me_4H$) by treating a toluene solution of $Cp^{Me4}{}_2UCl_2$ with MeLi, followed by stirring for 10 hours and centrifugation to remove

LiCl and black insoluble solids.[41] $(Cp^{Me4SiMe3})_2UMe_2$ ($Cp^{Me4SiMe3}$ = $\eta^5$-$C_5Me_4SiMe_3$) was synthesized similarly from $(Cp^{Me4SiMe3})_2UCl_2$ and MeLi, but required a reaction time of 12 hours. Kiplinger and co-workers synthesized $Cp^{Me4Et}{}_2UMe_2$ ($Cp^{Me4Et}$ = $\eta^5$-$C_5Me_4Et$) by treating a diethyl ether/dioxanes solution of $Cp^{Me4Et}{}_2UCl_2$ with MeMgBr dropwise, followed by stirring for 16 hours and filtration to remove magnesium salts.[42]

$^1H$ NMR spectroscopic and structural data for the family of bis($Cp^X$) 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, $Cp^{Me4Et}$, 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 $^t$butyl congener. The U-C bond distances for the methyl groups range from 2.37(3) to 2.429(4) Å, serving as a reference value for other uranium(IV)-$C_{alkyl}$ bonds.

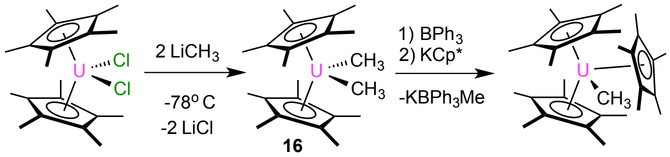
**Table 1.** Spectroscopic and structural data for $Cp^X{}_2UMe_2$ derivatives.

| Compound | $U-CH_3$ Resonance $^1H$ NMR Spectroscopy (ppm) | $U-CH_3$ Distance (Å) |
|---|---|---|
| $(Cp^{Me4Et})_2UMe_2$ | -137.2 | 2.429(4) |
| | | 2.415(4) |
| $Cp^*{}_2UMe_2$ | -124 | 2.424(7) |
| | | 2.414(7) |
| $(Cp^{Me4SiMe3})_2UMe_2$ | -123.27 | 2.425 |
| $(Cp^{tBu3})_2UMe_2$ | -98 | 2.37(3) |
| $Cp^{Me4}{}_2UMe_2$ | -73.5 | 2.426(2) |
| $Cp^{‡}{}_2UMe_2$ | -35.43 | -- |
| $Cp''UMe_2$ | -21.03 | 2.42(2) |

Isolation of the uranium(IV) trialkyl, $Cp^*U(CH_2Ph)_3$, was recently performed by reaction of $Cp^*UCl_3$ and $LiCH_2Ph$ in THF at -78° C[43] or from *in situ* reaction of $UCl_4$ and MgClCp* in toluene/dioxanes at ambient temperature, followed by addition of 3 equivalents of $MgCl(CH_2Ph)$.[44] Similarly, the $(Cp')_3UR$ (Cp' = $\eta^5$-$Me_3SiC_5H_4$; R=Me, $^n$Bu, $CH_2SiMe_3$, $CH_2Ph$, CCPh, $CHCH_2$ (Figure 3)) family was synthesized in an analogous fashion with alkyllithium reagents.[45]

The alkyl groups in these Cp-based uranium alkyl compounds are subject to further reactivity. For instance, the benzyl groups in $Cp^*U(CH_2Ph)_3$ readily undergo protonation, thus adding 2 equivalents of cyclopentadiene yields the mixed Cp compound, $Cp^*Cp_2U(CH_2Ph)$, and two equivalents of toluene.[44] Methyl abstraction can be accomplished by treating a toluene solution of $Cp^*{}_2UMe_2$ with $BPh_3$, forming $[Cp^*{}_2UMe][MeBPh_3]$.[46] Subsequent addition of KCp, KCp*, or $KCp^{Me4}$ generates the tris(cyclopentadienyl) uranium(IV) alkyls, $Cp^*{}_2CpUMe$,[47] $Cp^*{}_3UMe$[46], or $Cp^*{}_2Cp^{Me4}UMe$, respectively (eq. 4).[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, $Cp^*{}_2U[\eta^2$-(N,N′)-R-N-N=$CPh_2]_2$ (R = $CH_3$, $PhCH_2$].[48]

**Eq. 4.** Synthesis of $Cp^*{}_2UMe_2$ **(16)** and $Cp^*{}_3UMe$.



**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 σ-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, $((3,5-Me_2C_6H_3)N^tBu)_3UI$, affords $((3,5-Me_2C_6H_3)N^tBu)_3UCH_3$ (**17**) (Figure 4). Isolation is possible after stirring for one hour at room temperature followed by pentane extractions and filtration to remove LiI.[49] Crystallographic characterization showed a U-C distance of 2.466(7) Å, close to that reported for $Cp^*{}_2UMe_2$ but shorter than the uranium(III) compounds. Similarly, Behrens et al. used chelating NCN ligands to stabilize uranium(IV) alkyls. To ($p$-$RC_6H_4C(NSiMe_3)_2)_3UCl$ was added an equivalent of MeLi in diethyl ether at -100° C. Warming to room temperature over 12 hours produced tetravalent ($p$-$RC_6H_4C(NSiMe_3)_2)_3UMe$ (R= H (**18**) (Figure 4), $CF_3$ (**19**), OMe (**20**)) with loss of LiCl.[50] These derivatives were characterized by mass spectrometry, and resonances for the σ-bonded methyl substituents were visible in the $^1H$ NMR spectrum (benzene-$d_6$) 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 $Cp^{‡}{}_2UMe_2$. 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) Å. The olive green dimethyl derivative, $[(2,4,6-(CF_3)_3C_6H_2C(NSiMe_3)_2]_2UMe_2$ was generated by addition of two equivalents of methyllithium 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 $^1H$ NMR spectrum for the two equivalent methyl groups, within error of the mono(methyl) derivative.

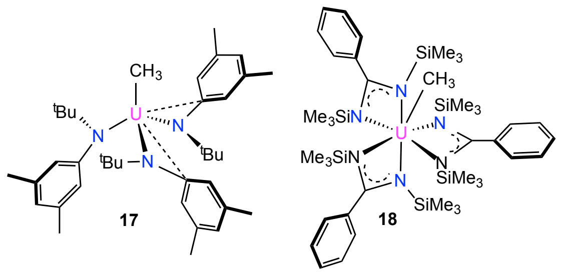
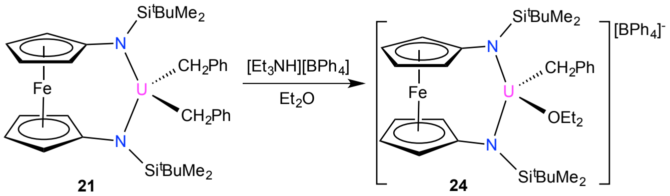


**Figure 4.** Non-Cp Uranium (IV) alkyls: ((3,5-$Me_2C_6H_3$)N$^t$Bu)$_3$$UCH_3$ (**17**) (left), (*p*-H-$C_6H_4C(NSiMe_3)_2)_3$UMe (**18**) (centre), and $LiUCH_3(OCH(CMe_3)_2)_4$ (**27**) (right).

In 2008, Diaconescu and co-workers began exploring the use of ferrocene diamides, fc($NSiRMe_2)_2$, as redox-active supports for uranium(IV) alkyls. Using a cooled suspension of fc($NSiRMe_2)_2UI_2$(THF) 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($NSiRMe_2)_2UBn_2$ (R= $^t$Bu (**21**)[51], Ph (**22**)[52]). $^1$H NMR spectroscopic analysis of **21** showed a far upfield resonance at -154.46 ppm for the methylene protons (benzene-*d$_6$*), on the order of those for $(Cp^{Me4Et})_2UMe_2$, 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 = $^t$Bu, Ph, Me (**23**)) 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 $[Et_3NH][BPh_4]$. Stirring at room temperature and recrystallizing from toluene and diethyl ether affords the cation-anion pair, [fc(NSi$^t$BuMe$_2$)$_2$UBn($OEt_2$)][$BPh_4$] (**24**) (eq. 5). Crystallographic data obtained for **24** showed a pseudotetrahedral uranium centre with an $\eta^2$-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 $\mu_B$ for **24** vs. 3.2 $\mu_B$ (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 intra- and intermolecular alkyne hydroamination[54] and mediates aromatic heterocycle activation with a variety of substrates.[55-58]

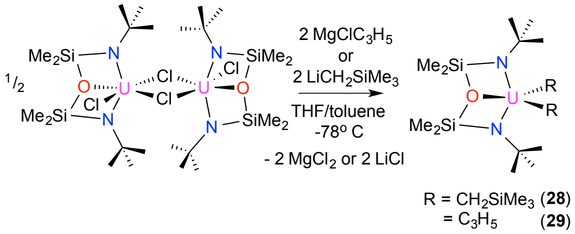


**Eq. 5**. Protonation of a benzyl group on fc(NSi$^t$BuMe$_2$)$_2$UBn$_2$ (**21**) by $[Et_3NH][BPh_4]$, forming [fc(NSi$^t$BuMe$_2$)$_2$U-Bn($OEt_2$)][$BPh_4$] (**24**).

Both **21** and **23** can be made by *in situ* reaction of $UI_3(THF)_4$ with 3 equivalents of benzyl potassium, presumably generating $U(CH_2Ph)_3(THF)_x$, followed by 0.75 equivalents of fc($HNSiRMe_2)_2$ in toluene and diethyl ether at -78°C.[59] Variation of the alkyllithiuim is possible, thus fc(NSi$^t$BuMe$_2$)$_2$U($CH_2SiMe_3)_2$ (**25**) and fc(NSi$^t$BuMe$_2$)$_2$U-($CH_2CMe_3)_2$ (**26**) have also been isolated. The latter synthetic strategy is effectively applied to the 2,6-bis(2,6-diisopropylanilidomethyl)pyridine ligand (NN$^{py}$), affording (NN$^{py}$)U($CH_2Ph)_2$, whereas using only 2 equivalents of $KCH_2Ph$ generates the monobenzyl species, (NN$^{py}$)U($CH_2Ph$)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 $U(OCH(CMe_3)_2)_4$ with MeLi (1 equivalent in hexanes) to produce five coordinate $LiUCH_3(OCH(CMe_3)_2)_4$ (**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-*d$_6$*) in the $^1$H 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.

Ether 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, [$^{tBu}$NON]$^{2-}$ = (($CH_3)_3CN(Si(CH_3)_2)]_2O$ and $^{DIPP}$NCOCN = (((2,6-$^i$Pr$_2C_6H_3$)N($CH_2CH_2))_2O$). Synthesis of ($^{tBu}$NON)$UR_2$ (R = $C_3H_5$ (**28**) or $CH_2(SiMe_3)$ (**29**)) can be achieved either by adding 4 equivalents of $MgClC_3H_5$ or $LiCH_2SiMe_3$ in toluene/THF at



**Eq. 6** Synthesis of ($^{tBu}$NON)$UR_2$ alkyls (**28-29**).

-78° C[61] to dimeric ((${}^{tBu}$NON)UCl$_2$)$_2$ or by treating (${}^{tBu}$NON)UI$_3$Li(THF)$_2$ with 2 equivalents of LiCH$_2$(SiMe$_3$) in toluene at -30° C (eq. 6).[62] While no crystallographic evidence could be obtained for either compound, $^1$H NMR studies confirmed the $\eta^1$-coordination of the allyl ligand in **28**, with the methine resonance appearing at 72.84 ppm (toluene-$d_8$). The positive shift of this resonance is similar to that observed for Cp$_3$U(allyl) (**13**), but is opposite those of the methyl resonances in the Cp$^X{}_2$UMe$_2$ family, which all have negative chemical shift values. The shift of the methylene (-148.9 ppm) protons in **29** is in line with the Cp$^X{}_2$UMe$_2$ family. The tetravalent alkyls, (${}^{DIPP}$NCOCN)UR$_2$, are synthesized from (${}^{DIPP}$NCOCN)UCl$_2$ with 2 equivalents of LiCH$_2$SiMe$_3$[62] (**30**) or KCH$_2$Ph[63] (**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 $\eta^1$- and $\eta^2$-coordinated benzyl groups, with respective U-C distances of 2.483(14) and 2.544(13) Å. Resonances for the respective $\eta^1$ and $\eta^2$-benzyl methylene protons are observed at -125.92 and -73.46 ppm by $^1$H NMR spectroscopy (benzene-$d_6$), 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, 4,5-bis(2,6-diisopropylanilino)-2,7-di-*tert*-butyl-9,9-dimethylxanthene) = XA$_2$, to stabilize analogous species. To (XA$_2$UCl$_3$)(K(dme)$_3$), 2 equivalents of an alkyllithium are added in hexane at -78° C and the reaction mixture warmed to room temperature over 12 hours, producing XA$_2$UR$_2$ (R= CH$_2$SiMe$_3$ (**32**) or CH$_2$CMe$_3$ (**33**) (Figure 5)). Compound **33** was also generated by treating **32** with 2.1 equivalents of neopentyllithium with concurrent elimination of LiCH$_2$SiMe$_3$. **32** shows a fluxional molecule at 25° C by $^1$H 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-$d_8$) for the methylene protons, indicating a $C_s$ symmetric molecule, which is confirmed crystallographically. The U-C distances range from 2.368(7) – 2.418(7) Å; **33** shows analogous distances. The $^1$H NMR spectrum for **33** has very broad resonances assignable to the methylenes 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 SiMe$_4$ or CMe$_4$. Adding 1.3 equivalents of LiCH$_2$SiMe$_3$ to **32** creates the charged pair, (XA$_2$U(CH$_2$(SiMe$_3$))$_3$)(Li(THF)$_x$), characterized by resonances at 314.6, 268.8, and -161.0 in the $^1$H NMR spectrum (THF-$d_8$) for the methylene protons, which shift to 451.0, 378.0, and -236.9 ppm at -75° C. Isolation of the trimethyl 'ate' complex (XA$_2$UMe$_3$)(Li(dme)$_3$) (**34**) (Figure 5) was possible by adding 3.3 equivalents of MeLi to (XA$_2$UCl$_3$)(K(dme)$_3$) in dme, followed by extraction with toluene to remove KCl and LiCl.[64] 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 $^1$H NMR spectrum for the methyl groups between +400 and -400 ppm (THF-$d_8$) for the THF analogue, (XA$_2$UMe$_3$)(Li(THF)$_x$).

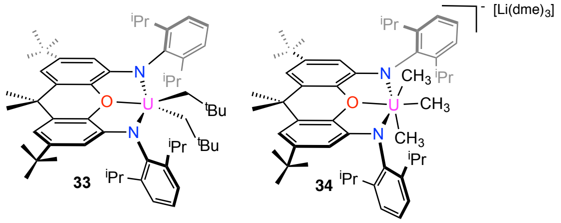


**Figure 5.** The uranium(IV) bis(alkyl), XA$_2$U(CH$_2{}^t$Bu)$_2$ (**33**), and the uranium(IV) trimethyl anion, [XA$_2$UMe$_3$][Li(dme)$_3$] (**34**).

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(IV) alkyls.[65] To (dmpe)$_2$UCl$_4$, addition of 4 equivalents of MeLi at -20° C in diethyl ether proceeded to brown-yellow (dmpe)$_2$UMe$_4$ (**35**).[65, 66] Analysis by $^1$H NMR spectroscopy at -70° C in toluene-$d_8$ shows an intense singlet at 10.1 ppm for the equivalent methyl groups, but no such resonance was visible by $^{13}$C 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)$_4$U(dmpe)$_2$ and toluene. Shores and co-workers recently performed further characterization on **35**,[66] 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 $\mu_B$ (300 K – 2 K), respectively.[53] 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 benzyllithium at -70° C, which generates (dmpe)U(CH$_2$Ph)$_4$ (**36**).[67] This was recently crystallographically characterized by our group, and showed a distorted trigonal prismatic uranium centre for the U-C and U-P σ-bonds.[68] The U-C distances range from 2.460(9) to 2.523(8) Å, supporting each benzyl group is coordinated in an $\eta^4$-fashion. Performing $^1$H 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 $C_s$ symmetric molecule at this temperature. The magnetic moment at 23° C was reported to be 2.70 $\mu_B$,[24] lower than that for **35**, but still on the order of uranium(IV) compounds. Using a 3:1 ratio of benzyllithium to methyllithium in the analogous reaction creates the mixed alkyl product, (dmpe)U(CH$_3$)(CH$_2$Ph)$_3$ (**37**).[67] Andersen reports the benzylic 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 benzylic carbanion, which lowers the electron density at the $sp^3$ hybridized carbon. As in the case of **36**, the benzyl substituents in **37** have structural parameters consistent with $\eta^4$-bonding.

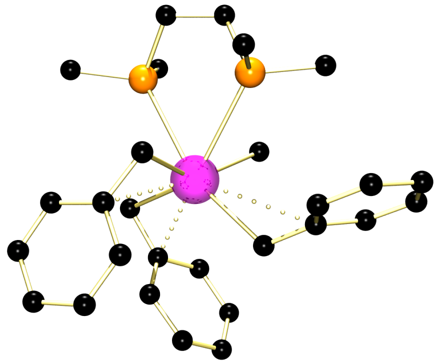


**Figure 6.** Solid state structure of Andersen's (dmpe)$UCH_3(CH_2Ph)_3$ (**37**).

**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 $UCl_4$ with four equivalents of various alkyllithium reagents (LiR, R = Me, $^{i}$Pr, $^{n}$Bu, $^{t}$Bu, neopentyl, 2-*cis*-2-butenyl, 2-*trans*-2-butenyl) in NMR tube experiments at -78$^{o}$ C resulted in the desired salt metathesis. [8, 69] However, upon warming, the $UR_4$ 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 $UCl_4$ was treated with 4 equivalents of LiR (R = $^{n}$Bu, $^{t}$Bu) followed by stirring for 5-6 days, the desired tetravalent uranium alkyls were not formed but rather a reduced trivalent uranium hydride was proposed.[70]

Generation of isolable homoleptic uranium(IV) alkyls has been achieved by the formation of 'ate' complexes. Wilkinson and Sigurdson first reported that treating $UCl_4$ with excess LiR produced the tetravalent uranate compounds $[Li(solvent)_4]_2[UR_6]$ (solvent = THF, $Et_2O$; R = Me, $C_6H_5$, *o*-$PhCH_2NMe_2$, $CH_2SiMe_3$) and in the presence of TMEDA (TMEDA = *N,N,N',N'*-tetramethylethylenediamine), $Li_2UR_6$•7TMEDA.[9] Both elemental analysis and NMR studies carried out at temperatures below 0$^{o}$ C identified the proposed compounds by their integration values, and it was suggested that these anionic complexes were those initially studied by Marks.[9] More recently, however, additional studies have called the identity of the molecules proposed by Wilkinson into question.[71]

Hayton and co-workers have reported a similar series of well-defined, uranium(IV) homoleptic anions. By adding 4.5 equivalents of $LiCH_2SiMe_3$ to $[Li(THF)]_2[U(O^{t}Bu)_6]$ and excess LiCl, the uranium(IV) salt, $[Li_{14}(O^{t}Bu)_{12}Cl][U(CH_2SiMe_3)_5]$ (**38**), was formed in low yields.[72] In this case, the $LiO^{t}Bu$ formed in the reaction is retained rather than removed. Characterization by $^{1}H$ NMR spectroscopy showed a singlet at 18.42 ppm (benzene-*d$_6$*) 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,[5, 73] Marks,[8] or Seyam.[8, 69] This inherent stability is attributed to the five bulky neosilyl ligands, which coordinatively saturate the uranium centre. However, rapid decomposition was noted in solution, due to the lability of the $[Li_{14}(O^{t}Bu)_{12}Cl]$ counterion. In an effort to produce more thermally stable compounds, $UCl_4$ was treated with 5 equivalents of an alkyllithium (LiR, R= $CH_2SiMe_3$, $CH_2{}^{t}Bu$) at -25$^{o}$ C, producing $[Li(DME)_3][U(CH_2SiMe_3)_5]$ (**39**) (from THF/ether/DME solution) and $[Li(THF)_4][U(CH_2{}^{t}Bu)_5]$ (**40**) (from THF/ether solution) in high yields, respectively. Compound **39** was identified by $^{1}H$ NMR spectroscopy, which showed the respective methyl and methylene proton resonances at -2.15 and 17.80 ppm (benzene-*d$_6$*/THF-*d$_8$*). 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 $UCl_4$ with 6 equivalents of MeLi in a solution of ether/tetrahydrofuran/TMEDA generated the U(IV) hexa(alkyl) complex $[Li(TMEDA)]_2[UMe_6]$ (**41**), which is only stable below -25° C. The $^{1}H$ NMR spectrum (THF-*d$_8$*) shows a

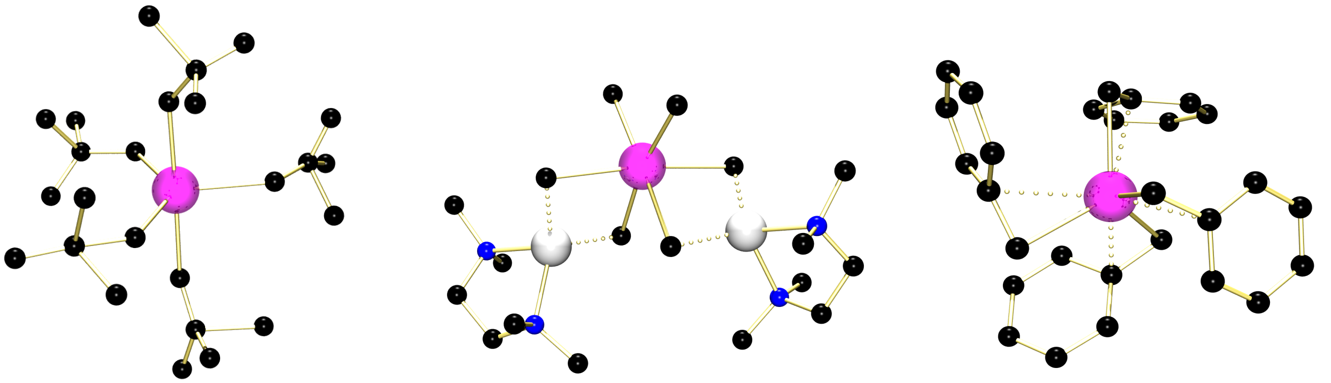
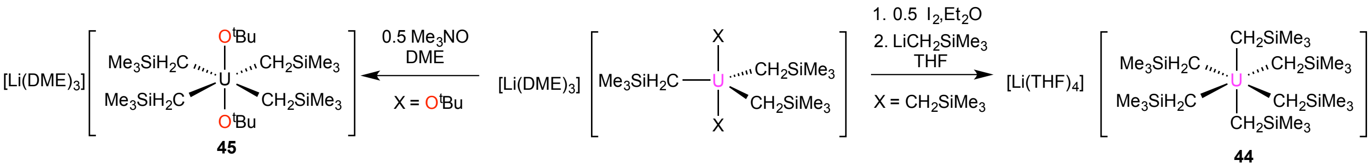


**Figure 7.** Solid state structure of the $[U(CH_2{}^{t}Bu)_5]$ anion in Hayton's $[Li(THF)_4][U(CH_2{}^{t}Bu)_5]$**(40)** (left) and homoleptic uranium(IV) $[Li(TMEDA)]_2[UMe_6]$ (**41**) (centre), as well as Bart's neutral homoleptic uranium(IV) tetra(alkyl), $U(CH_2Ph)_4$ (**43**) (right).



**Eqn. 7** Synthesis of uranium(V) alkyls at -25° C, $[Li(DME)_3][U(CH_2SiMe_3)_4(O^tBu)_2]$ (**45**) (left) and $[Li(THF)_4][U(CH_2SiMe_3)_6]$ (**44**) (right). Equation adapted from reference 76.

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 2.48(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 $UCl_4$, generated $\{[K(THF)]_3[K(THF)_2][U(CH_2C_6H_5)_6]_2\}_x$ (**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-$d_6$/THF) in the $^1H$ NMR spectrum, on the order of that for **41** and $Cp''_2UMe_2$, 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. Tetrabenzyluranium, $U(CH_2Ph)_4$ (**43**), was synthesized by addition of 4 eq. $KCH_2Ph$ to $UCl_4$ at -108° C, followed by immediate filtration and workup in diethyl ether to remove KCl. The $^1H$ NMR spectrum (benzene-$d_6$) for **43** showed a resonance at -30.41 ppm for the methylene protons, similar to **42** and $Cp^{\ddagger}_2UMe_2$. The respective *p*-tolyl and *m*-xylyl derivatives, $U(CH_2\text{-}p\text{-}CH_3C_6H_4)_4$ and $U(CH_2\text{-}m\text{-}(CH_3)_2C_6H_3)_4$, 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 $U(CH_2\text{-}p\text{-}CH_3C_6H_4)_4$ appears at -30.42 ppm and that for $U(CH_2\text{-}m\text{-}(CH_3)_2C_6H_3)_4$ is visible at -23.74 ppm. Characterization of **43** by X-ray crystallography shows U-C σ-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 in solution at ambient temperature for one hour, after which time they begin to decompose, mainly by U-C homolytic scission. In contrast to the $UR_4$ derivatives by Marks and Seyam, stability of these species is conferred by the bulky benzyl groups, which coordinate in an $\eta^4$-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,[68, 74] 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.[74]

## 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.[75] As a result, aside from the penta(halide) 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.[76] In recent years, advanced experimental and computational techniques have helped highlight the potential role of pentavalent species in Nature and in separations processes.[75] Currently, neutral pentavalent uranium centres with σ-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 $[Li(dioxane)]_3[UR_8]$.[9] Starting with uranium(V) pentaethoxide in light petroleum, an excess of LiR (R = $CH_3$, $CH_2SiMe_3$, $CH_2CMe_3$) 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-$d_5$). Treating these species with alcohols protonates the U-C bond, forming the corresponding alkoxide 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.[77] Oxidation of the corresponding U(IV) penta(alkyl) compound, $[Li(DME)_3][U^{IV}(CH_2SiMe_3)_5]$ (**39**), with 0.5 equiv $I_2$ in $Et_2O$ at -25° C, followed by salt metathesis using 1 equiv of $Li(CH_2SiMe_3)$, furnished pentavalent $[Li(THF)_4][U(CH_2SiMe_3)_6]$ (**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-$d_8$), 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 $LiCH_2SiMe_3$ to THF solutions of $[Li(THF)_4][U(CH_2SiMe_3)_6]$ 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 $f^1$ 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.[78] The magnetic moment of 1.54 $\mu_B$ at 300 K,[53] is smaller than the 2.54 $\mu_B$ calculated for the $U^{5+}$ ion in a $^2F_{5/2}$ ground state,[79] but comparable to the value for $[Li(DME)_3][U(NC_5H_{10})_6]$ (1.3 μB).[80] At 4 K, the observed value is 1.19 $\mu_B$, eliciting a temperature response previously observed for U(V).[79, 81-84] 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.

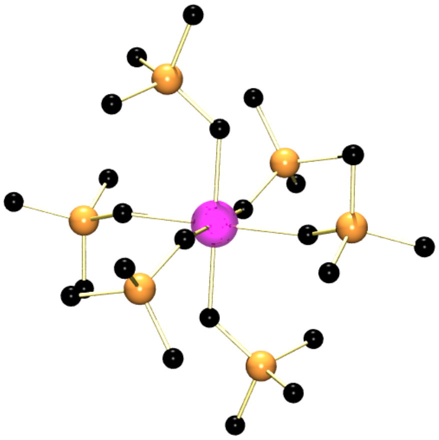


**Figure 8.** Solid state structure of Hayton's $[U(CH_2SiMe_3)_6]^-$ anion (**44**). The lithium counter cation, $[Li(THF)_4]^+$, has been removed for clarity.

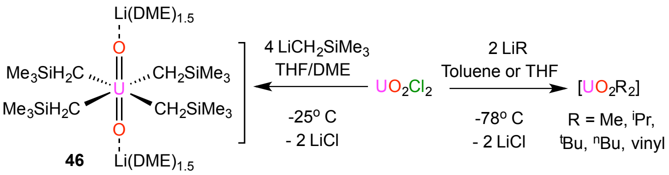
**4.2 Alkoxide supported alkyls:** Hayton has also demonstrated monodentate alkoxide ligands are effective ancillary ligands to support organouranium(V) species. Addition of 0.5 equiv. $Me_3NO$ to $[Li(DME)_3]$-$[U^{IV}(CH_2SiMe_3)_3(O^tBu)_2]$ in DME at -25°C produced the uranium(V) alkyl derivative, $[Li(DME)_3]$-$[U(CH_2SiMe_3)_4(O^tBu)_2]$ (**45**) in moderate yield (43%) (eq 7).[77] Analysis by $^1H$ NMR spectroscopy (THF-$d_8$) showed a resonance at -0.38 ppm for the equivalent methylene protons, just upfield of the homoleptic anion **44**. Compound **45** is more thermally stable than its homoleptic counterpart, indicating the alkoxy 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.[53]

## 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 dioxouranium(VI) complexes.[85] Starting from $UO_2Cl_2$ in either toluene or THF, 2 equivalents of LiR or MgClR' (R = $CH_3$, $^nBu$, $^tC_4H_9$, $C_6H_5$; R' = $CH_2CH_2$, $^iC_3H_7$) were added at -78° C (eq. 8). These compounds are thermally unstable, decomposing at ambient temperature to afford "$UO_2$" 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 $Li(CH_2SiMe_3)$ in DME results in formation of green $[Li(DME)_{1.5}]_2[UO_2(CH_2SiMe_3)_4]$ (**46**), which is thermally sensitive and decomposes at room temperature in a few hours (eq. 8).[86] 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 $^{13}C$ 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 $[U(CH_2SiMe_3)_6]$ (*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, $[Li(DME)_{1.5}]_2[UO_2(CH_2SiMe_3)_4]$ (**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.[87] Starting from $U^{IV}Me(N(SiMe_3)_2)_3$ in diethyl ether at -21° C, N-methylmorpholine-N-oxide is used as an oxidant to form dark red $U^{VI}(O)Me(N(SiMe_3)_2)_3$. Interestingly, solutions of $U^{VI}(O)Me(N(SiMe_3)_2)_3$ 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 $^{13}C$ 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.[77] Formation of a stable hexavalent species was predicted by electrochemical oxidation of $[Li(THF)_4][U^V(CH_2SiMe_3)_6]$. Addition of $U(O^tBu)_6$, a mild chemical oxidant, to $[Li(DME)_3][U^V(CH_2SiMe_3)_6]$ in THF at -25° C forms neutral deep gold $U^{VI}(CH_2SiMe_3)_6$ (**47**) and $[Li(THF)_x][U(O^tBu)_6]$. Thus, assignment of **47** is supported by resonances in the $^1H$ NMR spectrum (THF-$d_8$, -40° C) at -3.15 and 0.52 ppm in a 2:9 ratio for the methylene and methyl resonances, respectively, and by resonances at 434.3 and 11.12 ppm, for the methylene and methyl carbons of the neosilyl ligand in the $^{13}C(^1H)$ NMR spectrum (THF-$d_8$, -46° C), respectively. Although **46, 47,** and $U^{VI}(O)Me(N(SiMe_3)_2)_3$ are diamagnetic, the extreme chemical shifts of their protons are are attributed to relativistic spin–orbit (SO) coupling.[86] 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 Cyclometallation of Silyl Substituents:** Sattelberger and co-workers observed an early example of a cyclometallated uranium(IV) alkyl, $Cp^*_2U(CH_2SiMe_2)PSiMe_3$ (**48**), by C-H activation of $SiMe_3$ in $Cp^*_2U(CH_3)P(SiMe_3)_2$ upon heating to 120° C in benzene (Figure 9). Concurrent with its formation is release of methane.[88] 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 $Cp^*_2UMe_2$.

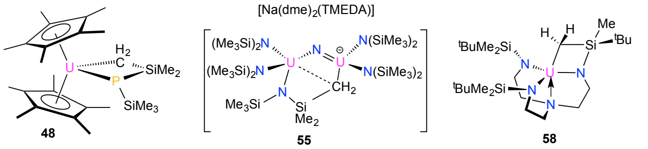
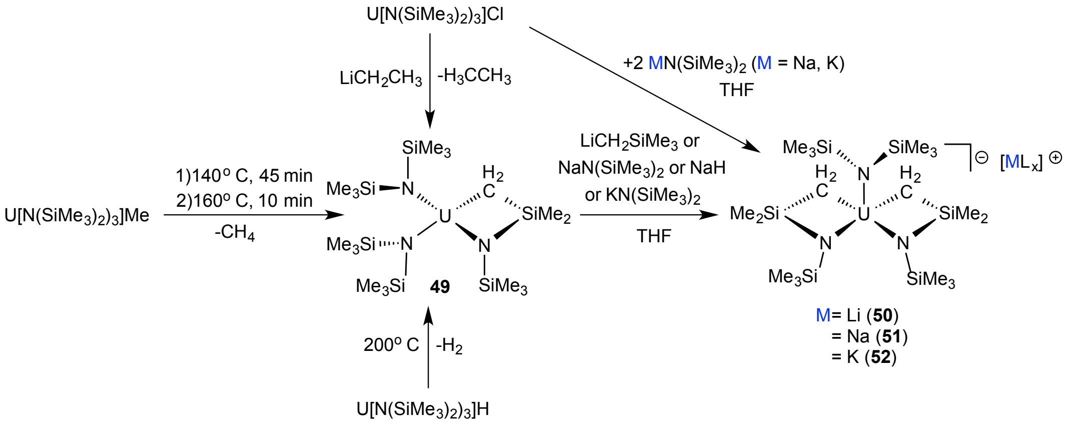


**Figure 9.** Cyclometallated uranium alkyls species, **49** (left), **55** (centre), and **58** (right).

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 $[(Me_3Si)_2N]_3UMe$ 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 $[(Me_3Si)_2N]_3UCl$ in pentane at 0° C with an equivalent of LiEt in toluene (0.47 M), followed by stirring at 0°C for 16 hours.[89] This forms "$[(Me_3Si)_2N]_3UEt$", which avoids β-hydrogen elimination by cyclometallating to form **49** and ethane. Compound **49** can also be formed through

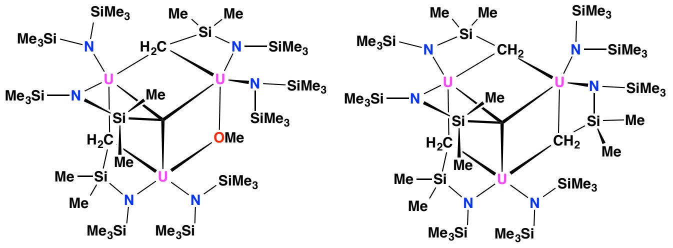


**Eq. 9.** Synthesis and reactivity of **49**.

pyrolysis of solid $[(Me_3Si)_2N]_3UH$ 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-$d_6$) 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, $[ML_x][UN(SiMe_3)_2(CH_2SiMe_2NSiMe_3)_2]$ (M = Li (**50**), Na (**51**), K (**52**); L= THF or crown ethers) (eq. 9).[90] Treating $[(Me_3Si)_2N]_2U(CH_2SiMe_2NSiMe_3)$ (**49**) with $LiCH_2SiMe_3$ formed **50**, with $Na(N(SiMe_3)_2)$ or NaH formed **51**, and with $K(N(SiMe_3)_2)$ formed **52**. Alternatively, **51** and **52** can be made directly by treating $UCl_4$ with 5 equivalents of $NaN(SiMe_3)_2$ or $KN(SiMe_3)_2$, respectively. Substitution of L is achieved through heating $[ML_x]$-$[UN(SiMe_3)_2(CH_2SiMe_2NSiMe_3)_2]$ in the desired solvent. For the THF analogue of **51** and **52**, the $^1H$ NMR spectra (THF-$d_8$) were identical, showing resonances for the protons of the methylenes coordinated to uranium at -286.20 and -297.80 ppm. All of these are similar in chemical shift to **48,** and using 15-crown-5 to chelate the Na in **51** produced a negligible chemical shift in this resonance. The corresponding U-C distances for one of the molecules of the THF analogue in the asymmetric unit are 2.467(6) and 2.506(6) Å, while those for **52** are the same within error at 2.532(4) and 2.506(5) Å (Figure 11). The metallacyclic U-C bond in **51** readily undergoes a 1,2-insertion of carbon monoxide and carbon dioxide, driven by formation of strong uranium-oxygen bonds.[90]

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.[91] Addition of $LiCH_2SiMe_3$ to $UCl_2(N(SiMe_3)_2)_2(DME)$ in hexane at ambient temperature produced the trinuclear cluster, $\{U[(\mu\text{-}CH_2SiMe_2)N(SiMe_3)][N(SiMe_3)_2]\}_2\{U[(\mu^3\text{-}C\text{-}SiMe_2)N(SiMe_3)][N(SiMe_3)_2]\}\{\mu\text{-OMe}\}$ (**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, $\{U[\mu\text{-}(CH_2SiMe_2)N(SiMe_3)][N(SiMe_3)_2]\}_2\{U[(\mu^3\text{-}C\text{-}SiMe_2)N(SiMe_3)][(\mu\text{-}CH_2SiMe_2)N(SiMe_3)]\}$ (**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**.



53

54

**Figure 10.** Gambarotta's trinuclear clusters (**53**) (left) and (**54**) (right).

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 $NaN_3$ to $U(N(SiMe_3)_2)_3$ created a dinuclear U(IV) cyclometallated bridging nitrido, $[Na(DME)_2(TMEDA)][(N(SiMe_3)_2)_2U(\mu\text{-}N)(CH_2SiMe_2N\text{-}(SiMe_3)U(N(SiMe_3)_2)_2]$ (**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 $I_2$ created the mixed-valent U(IV/V) nitrido dimer, $(N(SiMe_3)_2)_2U(\mu\text{-}N)(CH_2SiMe_2N(SiMe_3)U(N(SiMe_3)_2)_2$ (**56**) by elimination of

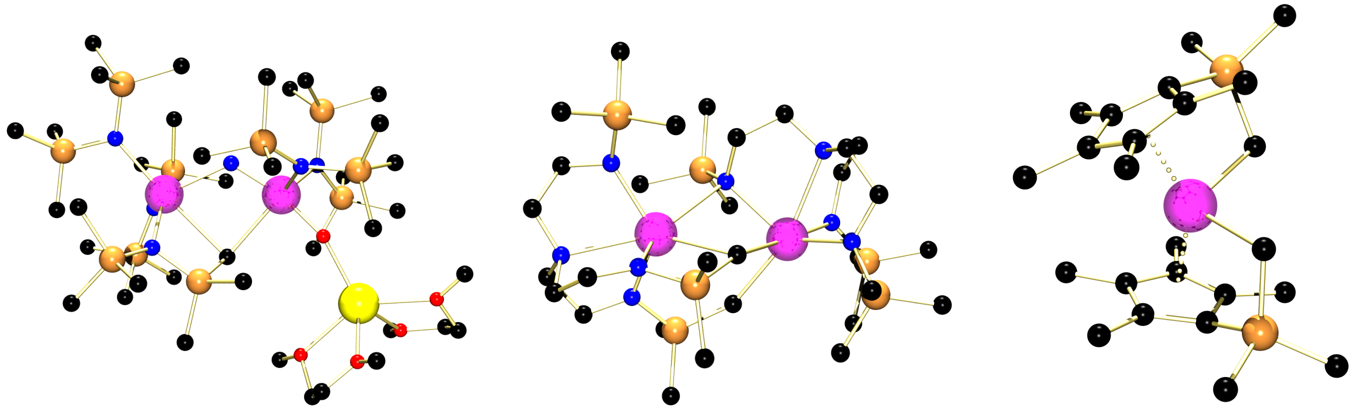


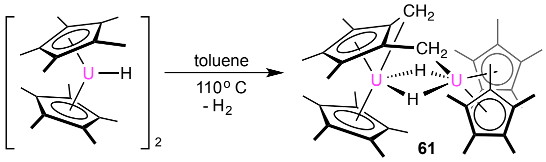
**Figure 11.** Solid state structures of Hayton's $[Na(DME)_2][(N(SiMe_3)_2)_2(O)U(\mu\text{-}N)(\textit{C}H_2SiMe_2N(SiMe_3)U(N(SiMe_3)_2)_2]$ (**57**) (left), Liddle's "tuck-in-tuck-over-tuck-over", $[U\{N(CH_2CH_2NSiMe_3)(CH_2CH_2NSiMe_2\textit{C}H_2)(CH_2CH_2NSiMe_2\text{-}\mu\text{-}\textit{C}H_2)\}U\{N(CH_2CH_2NSiMe_3)_3\}]$ (**59**) (centre), and Evan's "tuck in" $[(\eta^5:\eta^1\text{-}C_5Me_4SiMe_2CH_2)_2U]$ (**62**) (right).

NaI. 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 $\alpha$-carbon are visible at -76.74 ppm in the $^1H$ NMR spectrum. Oxidation of **55** with 1 equivalent of trimethylamine-*N*-oxide generates the mixed U(VI/IV) oxo species, $[Na(DME)_2][(N(SiMe_3)_2)_2(O)\text{-}U(\mu\text{-}N)(\textit{C}H_2SiMe_2N\text{-}(SiMe_3)U(N(SiMe_3)_2)_2]$ (**57**),[92] where again, the resonance for the methylene protons is not observed. The U-C distances highlight the asymmetric bridging of the methylene group at 2.598(9) and 2.74(1) Å. These derivatives are interesting examples of uranium alkyl species supported by multiply bonded ligands.

Scott and co-workers observed C-H bond activation for the methyl in $N(CH_2CH_2NSiMe_2{}^tBu)_3UI$ upon adding either KPh, $LiCH_2{}^tBu$ or $KCH_2Ph$, with extrusion of benzene, neopentane, or toluene,[92, 93] in analogy to Andersen. The cyclometallated product, $({}^tBuMe_2SiNCH_2CH_2)_2N(CH_2CH_2NSi{}^tBuCH_3\textit{C}H_2)U$ (**58**), features a remarkably long U-C bond of 2.752(11) Å, as well as C–H→U agostic interactions (Figure 9). The $^1H$ NMR spectrum supports the long uranium-methylene distance, as the resonances for the diastereotopic methylene protons appear at -35.34 and -52.34 ppm (toluene-$d_8$), far downfield from resonances with shorter U-C bonds such as those in **48**.

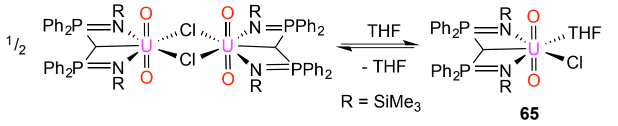
Liddle and co-workers found that adding $KCH_2Ph$ to $(N(CH_2CH_2NSiMe_3)_3)UI$ led to the formation of the yellow dinuclear "tuck-in-tuck-over-tuck-over" uranium(IV) complex, $[U\{N(CH_2CH_2NSiMe_3)(CH_2CH_2NSiMe_2\textit{C}H_2)(CH_2CH_2NSiMe_2\text{-}\mu\text{-}\textit{C}H_2)\}U\{N(CH_2CH_2NSiMe_3)_3\}]$ (**59**), by C-H activation (Figure 11). The uranium centres are bridged by a "tuck-over" methylene, which has U-C distances of 2.667(5) and 2.669(5) Å. Additionally, there is another terminal cyclometallated "tuck-in" uranium-methylene unit with U-C bond of 2.493(5) Å. The longer distance in the former can be attributed to the bridging nature, as compared to the terminal distance which is on the order of those for uranium(IV) alkyls. All predicted resonances were found in the $^1H$ NMR spectrum, but the complexity precluded assignment of the methylene protons proximal to uranium. Further reaction of this unusual cyclometallate with 2 equivalents of $[Et_3NH][BPh_4]$ generates the mononuclear "tuck-in" metallacycle, $[U(N(CH_2CH_2NSiMe_3)_2(CH_2CH_2NSiMe_2\textit{C}HBPh_2))]$ (**60**), where the methylene is capped by a diphenyl boron unit rather than another uranium centre as in the case of the starting material.[93] This reaction proceeds with extrusion of $NEt_3$, ½ $H_2$, PhH, and ½ $Ph_2$. The resonance for the methine proton appears at -59.4 ppm in the $^1H$ NMR spectrum (benzene-$d_6$), and this chemical shift is reflective of the elongated U-C distance of 2.644(9) Å, similar to the spectroscopic and structural data for **58**. In follow-up studies, treating the sterically more protected triisopropyl silyl-substituted analogue, $(N(CH_2CH_2NSi{}^iPr_3)_3)\text{-}UI$, with $KCH_2Ph$ produced the monomeric cyclometallated species, $[U(N(CH_2CH_2NSi{}^iPr_3)_2(CH_2CH_2NSi{}^iPr_2C[H]Me\text{-}\textit{C}H_2))]$,[94] which is analogous to Scott's **58**. Characterization by $^1H$ NMR spectroscopy showed a resonance at -1.33 ppm (benzene-$d_6$) for the methylene protons proximal to uranium, and a corresponding U-C distance of 2.55(2) Å as determined by X-ray crystallography. Computational studies determined that 5f-orbital stabilization of a $\sigma$-bond metathesis transition state for uranium played a key role in the observed cyclometallation chemistry.

**6.2 Cyclometallation by Organometallic Transformations:** Evans has recently reported several examples where cyclometallated uranium alkyl species form as a result of an initial reductive elimination process. For instance, reductive elimination of dihydrogen occurs upon heating $[Cp^*{}_2UH]_2$ in toluene to 110° C, generating a uranium (IV) double cyclometallated dimer, $[Cp^*U\{\mu\text{-}\eta^5:\eta^1:\eta^1\text{-}C_5Me_3(\textit{C}H_2)_2\}(\mu\text{-}H)_2UCp^*{}_2]$ (**61**) (eq. 10), from C-H bond activation.[95] In this case, adjacent methyl groups on the Cp* "tuck-in" and "tuck-over" to generate new uranium-methylene groups. The bridging hydrides were confirmed by infrared spectroscopy, which showed a large absorption at 1164 $cm^{-1}$ in the region typical for U-H-U stretching modes.[37, 96] The U-C distance for the "tuck-over" methylene that spans two uranium centres is 2.640(1) Å, while that for the "tuck-in" methylene is shorter at 2.564(1) Å. Both of these distances are longer than those typically observed for non-cyclometallated uranium(IV) species reported herein, 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=NPh, and cyclooctatetraene. Protonation of the uranium alkyl in **61** occurs upon addition of $D_2$, PhSH, and $PhNH_2$. Similarly, heating $(Cp^{Me4SiMe3})_2UMe_2$ in toluene to 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 $[(\eta^5{:}\eta^1\text{-}C_5Me_4SiMe_2\mathit{C}H_2)_2U]$ (**62**).[97] 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, $^i$PrN=C=N$^i$Pr, $CS_2$, and $N_3$Ad, or facile protonation with pyridine-N-oxide. Heating complexes of the form $Cp^*(C_8H_8)UR$ (R = Me, Ph) generates $(\eta^8\text{-}C_8H_8)(\eta^5{:}\eta^1\text{-}C_5Me_4\mathit{C}H_2)U$ (**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, $(\eta^8\text{-}C_8H_8)(\eta^5{:}\eta^1\text{-}C_5Me_4\mathit{C}H_2)U(THF)$ (**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 σ-bond in **63** readily undergoes 1,2-insertion of isonitriles, generating the iminoacyl uranium product.



**Eq. 10.** Formation of **61** via reductive elimination of dihydrogen.

**6.3 Uranium Methanide Complexes:** The first uranyl methanide compound, which features the U-C alkyl bond in a 6-membered metallacyle, was reported by Sarsfield in 2002.[99] Synthesis was accomplished by addition of one equivalent of $[Na(CH(Ph_2PNSiMe_3)_2)]_2$ to $UO_2Cl_2(THF)_3$, which afforded a deep red dimeric product, $[UO_2Cl(\mathit{C}H(Ph_2PNSiMe_3)_2]_2$, in good yield (eq. 11). The methine proton is observable at 2.52 ppm ($CD_2Cl_2$) 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, $UO_2Cl(\mathit{C}H(Ph_2PNSiMe_3)_2(THF)$ (**65**), which shows the methine proton at 2.28 ppm in thf-$d_8$, a carbon resonance at 19.5 ppm in the $^{13}$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 benzyl in THF results in reduction, producing the mixed valent uranium(V,VI) dimer, $[UO_2(\mathit{C}H(Ph_2PNSiMe_3)_2(\mu\text{-}Cl)UO(\mu\text{-}O)(\mathit{C}H(Ph_2PNSiMe_3)_2)]$, along with 0.25 equivalents of bibenzyl.[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-$d_6$). 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.



**Eq. 11.** Monomer-dimer equilibrium for uranium methanide complex **65**.

Ephritikhine has accomplished synthesis of mono- and bis(methanide) species, by treating $[UO_2(OTf)_2]$ with either one or two equivalents of $LiHC(Ph_2PS)_2$ in diethyl ether, respectively.[101] The mono(ligand) derivative, $[UO_2(\mathit{C}H(Ph_2PS)_2)(OTf)(OEt_2O)]$ (**66**), and bis(ligand) compound, $[UO_2(\mathit{C}H(Ph_2PS)_2)_2]$*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 $\sigma$-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 organuranium 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. $\alpha$-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 $\beta$-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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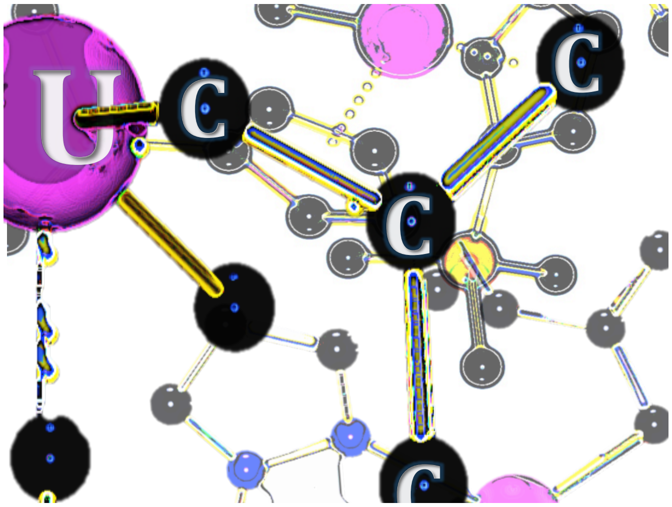
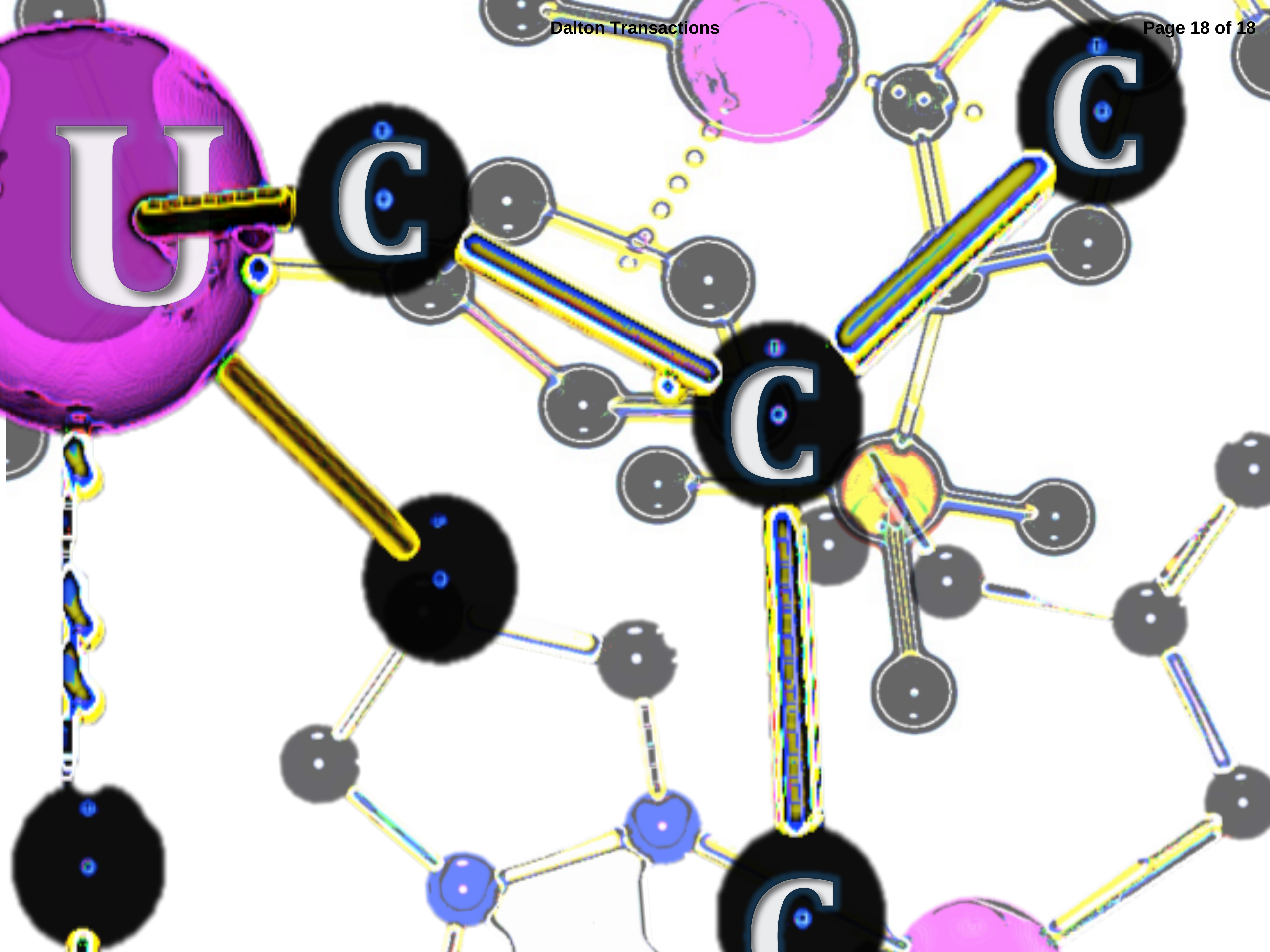
Table of Contents Entry

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

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