Synthesis and Characterization of two Uranyl-Aryl "Ate" Complexes

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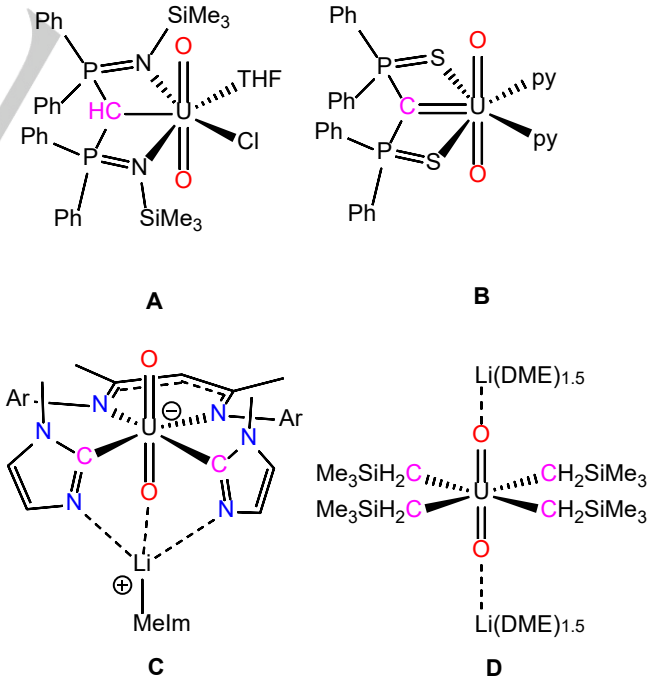
Abstract: Reaction of $[UO_2Cl_2(THF)_3]$ with 3 equiv of LiC_6Cl_5 in Et_2O resulted in the formation of first uranyl aryl complex $[Li(Et_2O)_2(THF)][UO_2(C_6Cl_5)_3]$ ([Li][**1**]) in good yields. Subsequent dissolution of [Li][**1**] in THF resulted in conversion to $[Li(THF)_4][UO_2(C_6Cl_5)_3(THF)]$ ([Li][**2**]), also in good yields. DFT calculations reveal that the U-C bonds in [Li][**1**] and [Li][**2**] exhibit appreciable covalency. Additionally, the ^{13}C chemical shifts for their C_{ipso} environments are strongly affected by spin-orbit coupling – a consequence of 5f orbital participation in the U-C bonds.

There are only a handful of uranyl complexes that feature direct uranium-carbon bonds, despite UO_2^{2+} being the most studied fragment in uranium chemistry.[1–4] Remarkably, the first attempt to make an organometallic uranyl complex was over 150 years ago;[5,6] however, the first structurally characterized uranyl hydrocarbyl complex was only reported by Sarsfield in 2002.[7] Earlier attempts to make uranyl organometallics often failed because of the reducing nature of many alkylating reagents. For example, reaction of $U^{VI}O_2Cl_2$ with 2 equiv of phenyllithium resulted in the formation of $U^{IV}O_2$ and biphenyl.[8,9] Similarly, reaction of $U^{VI}O_2I_2(THF)_3$ with KCp resulted in reduction to afford the pentavalent uranyl(V) fragment.[10]

In spite of the abovementioned challenges, several strategies have been developed in the last two decades to facilitate the formation of uranyl organometallic complexes.[7,11–24] For example, Sarsfield and co-workers stabilized the U-C bond in [(BIPMH)UO_2Cl(THF)] (**A**, BIPMH = $HC(PPh_2NSiMe_3)_2$) by utilizing a chelating bis(iminophosphorano)methanide ligand (Scheme 1).[7] This strategy was later used in the synthesis of the first uranyl carbene complex, $[UO_2(SCS)(py)_2]$ (**B**, SCS = $[C(Ph_2PS)_2]^{2-}$),[21] as well as the first uranyl η^5-pyrrole complex, $[Li(THF)][UO_2(L^{\Delta})Cl(THF)]$ (L^{Δ} = [Me_8-calix[4]pyrrole]$^{2-}$).[25] Another successful strategy involves formation of the uranyl fragment by oxygen atom transfer to a low-valent uranium cyclopentadienyl precursor.[13,16] In addition, our research group has utilized "ate" complex formation to stabilize uranyl-carbon bonds by saturation of the uranium coordination sphere, as exemplified by [Li(MeIm)][$(UO_2(Ar_2nacnac)(C_4H_5N_2)_2]$ (**C**)[24] and $[Li(DME)_{1.5}]_2[UO_2(CH_2SiMe_3)_4]$ (**D**) (Scheme 1).[23]

Recognizing that reduction of the uranium center was a major impediment to previous synthetic attempts, we attempted to ligate the percholorophenyl fragment, $[C_6Cl_5]^-$, to uranyl, because it is a much poorer reducing agent than most other alkylating agents, and thus should not as readily reduce the high-valent U^{6+} center in uranyl.[26] Homoleptic and heteroleptic perhalophenyl complexes are known for a wide variety of transition metals,[26–36] yet no reported perhalophenyl complexes are known for actinides, making this a potentially fruitful avenue of investigation. Herein, we describe the synthesis and characterization of the first structurally characterized uranyl aryl complexes, $[Li(Et_2O)_2(THF)][UO_2(C_6Cl_5)_3]$ ([Li][**1**]) and $[Li(THF)_4][UO_2(C_6Cl_5)_3(THF)]$ ([Li][**2**]). Additionally, we analyze their electronic structures and ^{13}C NMR spectra by relativistic density functional theory (DFT) calculations, which enabled us to identify the degree of participation of the 5f subshell in the uranium-carbon bonds.

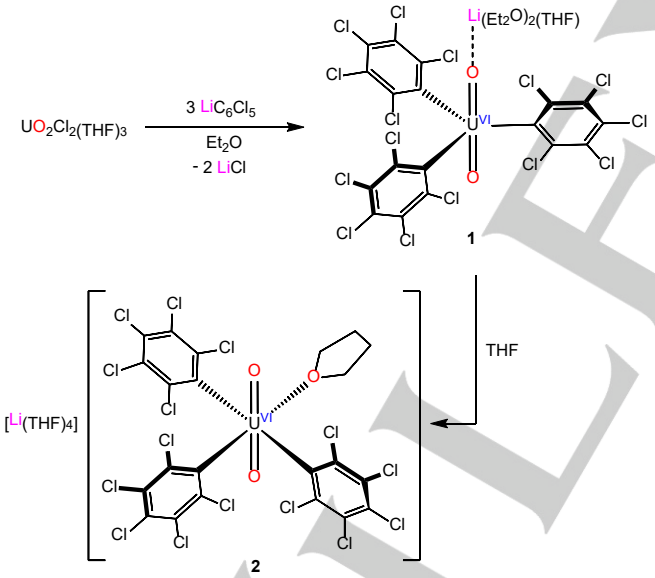


Scheme 1. Examples of uranyl complex with direct U-C σ bonds. MeIm = 1-methylimidazole, Ar = 2,6-$^{i}Pr_2C_6H_3$.

Addition of a cold (-25 °C) solution of 3 equiv of LiC_6Cl_5[37] to a cold (-25 °C) suspension of $[UO_2Cl_2(THF)_3]$[38] in Et_2O results in immediate formation of an orange solution, concomitant with the

deposition of a flocculent brown-orange precipitate. Work-up of this solution, followed by crystallization from Et_2O, affords $[Li(Et_2O)_2(THF)][UO_2(C_6Cl_5)_3]$ ([Li][**1**]), which can be isolated as orange plates in 74% yield (Scheme 2). Dissolution of complex [Li][**1**] in THF results in an immediate color change to dark amber. Crystallization of this solution affords $[Li(THF)_4][UO_2(C_6Cl_5)_3(THF)]$ ([Li][**2**]) as amber plates in 86% isolated yield (Scheme 2). Significantly, [Li][**1**] and [Li][**2**] are first structurally characterized uranyl aryl complexes, and are rare examples of crystallographically-authenticated uranyl organometallics.

Both [Li][**1**] and [Li][**2**] are moisture-sensitive crystalline solids that are soluble in ethereal solvents and benzene, but are insoluble in hexanes. Additionally, both decompose upon dissolution in pyridine. Surprisingly, complex [Li][**1**] displays good thermal stability in benzene-d_6 over the course of 24 h, according to $^{13}C\{^1H\}$ NMR spectroscopy (Figure S14). In contrast, both [Li][**1**] and [Li][**2**] completely decompose in THF-d_8 over this time frame (Figure S15). Prolonged exposure of [Li][**2**] to vacuum also results in significant decomposition, as evidenced by the observation of pentachlorobenzene (C_6Cl_5H) resonances in its $^{13}C\{^1H\}$ spectrum (Figure S15).[39] We surmise that the good thermal stability of [Li][**1**] in benzene-d_6 is partly a consequence of poor reducing ability of the $[C_6Cl_5]^-$ ligand; however, the *o*-chloro substitution also likely imparts increased kinetic stabilization relative to non-chlorinated aryl ligands, which can undergo facile *ortho*-CH activation.[40,41]



Scheme 2. Syntheses of $[Li(Et_2O)_2(THF)][UO_2(C_6Cl_5)_3]$ [Li][**1**] and $[Li(THF)_4][UO_2(C_6Cl_5)_3(THF)]$ [Li][**2**].

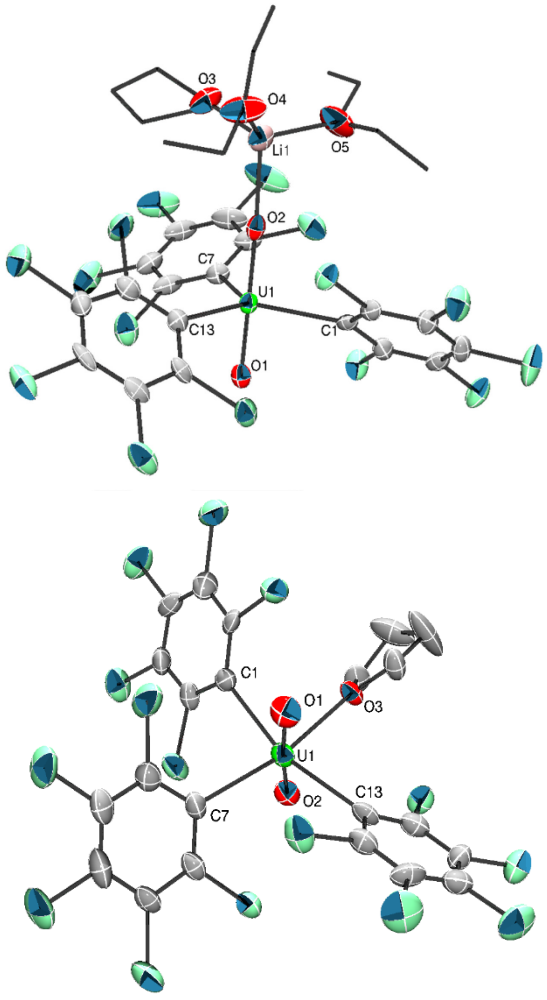


Figure 1. Solid-state molecular structure of [Li][**1**] (top) and [Li][**2**]·THF (bottom) shown with 50% probability ellipsoids. All hydrogen atoms, solvate molecules, and a $[Li(THF)_4]^+$ counterion have been omitted for clarity. Selected bond lengths (Å) and angles (°) for [Li][**1**]: U1-O1 = 1.750(5), U1-O2 = 1.779(5), U1-C1 = 2.484(7), U1-C7 = 2.471(8), U1-C13 = 2.489(8), O2-Li1 = 2.043(15), O1-U1-O2 = 178.7(2), C1-U1-C7 = 123.5(3), C7-U1-C13 = 119.0(3), C13-U1-C1 = 117.4(2). [Li][**2**]·THF: U1-O1 = 1.760(8), U1-O2 = 1.765(8), U1-O3 = 2.424(7), U1-C1 = 2.627(12), U1-C13 = 2.563(12), U1-C7 = 2.552(11), O1-U1-O2 = 173.7(4), C1-U1-C7 = 91.2(4), C7-U1-C13 = 106.6(4), C13-U1-O3 = 83.6(3), O3-U1-C1 = 78.7(3).

Both [Li][**1**] and [Li][**2**] (as the THF solvate, [Li][**2**]·THF) crystallize in the monoclinic space group $P2_1/n$ (Figure 1). The solid-state molecular structure of [Li][**1**] reveals a trigonal bipyramidal uranium center, coordinated by two oxygen atoms of the uranyl fragment and three carbon atoms of the pentachlorophenyl ligands. The solid-state molecular structure of [Li][**2**]·THF reveals a distorted octahedral uranium center, coordinated by two oxo ligands, three pentachlorophenyl ligands, and one THF ligand. Additionally, an $[Li(Et_2O)_2(THF)]^+$ cation is coordinated to a uranyl oxo ligand in complex [Li][**1**]. The O-U-O angles in [Li][**1**] (178.7(2)°) and [Li][**2**] (173.7(4)°) are typical of the uranyl fragment.[1],[3] Likewise, the U-O_{yl} bond lengths in [Li][**1**] (U1-O1 = 1.750(5), U1-O2 = 1.779(5) Å) and [Li][**2**] (U1-O1 = 1.760(8), U1-O2 = 1.765(8) Å) are typical of uranyl(VI) U-O_{yl} distances (1.76-1.79 Å).[1],[3] Curiously, coordination of Li^+ to an oxo ligand in [Li][**1**] does not result in any perturbation of the U-O_{yl} bond length, as both U-O_{yl} distances are within error, in

contrast to past examples of Lewis acid coordination.[23,42–44] These data suggest the Li-O_{yl} interaction is relatively weak, a suggestion which is further supported by the Li-O_{yl} bond length (2.043(15) Å), which is longer than typical Li-O_{yl} interactions (1.87(1) Å - 1.94(1) Å).[1,23,24,43,45] The U-C bond lengths in [Li][**1**] (range = 2.471(8) – 2.489(8) Å) are similar to those of other σ-bonded uranium-hydrocarbyl complexes. For example, the U-C distances in **C** are 2.498(6) Å and 2.499(7) Å, whereas those in **D** range from 2.497(6) to 2.481(6) Å.[15,23,24] In contrast, the U-C distances in [Li][**2**] (range = 2.552(11) – 2.627(12) Å) are somewhat longer, reflecting its higher coordination number. Finally, the U-C_{ipso}-C_{ortho} angles in [Li][**1**] and [Li][**2**] show minimal deviation from 120°, excluding the possibility of Cl→U dative interactions in the solid-state.

The $^{13}C\{^1H\}$ NMR spectrum of [Li][**1**] in benzene-d_6 features a resonance at 236.7 ppm (Figure S3), attributable to the *ipso* carbon of the pentachlorophenyl ligand, as well as resonances at 138.0, 134.2, and 132.4 ppm, assignable to the *ortho*, *meta*, and *para* resonances of the pentachlorophenyl ligand, respectively. Its $^7Li\{^1H\}$ NMR spectrum in benzene-d_6 features a sharp resonance at –3.34 ppm (Figure S2). The $^{13}C\{^1H\}$ NMR spectrum of [Li][**2**] in THF-d_8 features a resonance at 239.4 ppm (Figure S9), attributable to the *ipso* carbon of the pentachlorophenyl ligand, as well as resonances at 139.4, 133.6, and 130.5 ppm, assignable to the *ortho*, *meta*, and *para* carbons of the pentachlorophenyl ligand, respectively. The observation of only one aryl environment in this spectrum is evidence of reversible THF binding at a faster rate that the NMR time scale. Its $^7Li\{^1H\}$ NMR spectrum in THF-d_8 features a sharp resonance at –0.87 ppm (Figure S8). Curiously, the $^{13}C\{^1H\}$ NMR spectrum of [Li][**2**] in benzene-d_6 is nearly identical to that of [Li][**1**] in benzene-d_6, which is suggestive of dissociation of THF and reformation of [Li][**1**] in this solvent. Not surprisingly, the $^{13}C\{^1H\}$ NMR spectrum of [Li][**1**] in THF-d_8 features a similar C_{ispo} chemical shift as that of [Li][**2**] in the same solvent.

To gain a detailed understanding of the electronic structure and chemical bonding in [Li][**1**] and [Li][**2**], we carried out relativistic DFT calculations on the anionic components of these compounds, [**1**]$^-$ and [**2**]$^-$, respectively. Complete computational details for these calculations are given in the Supporting Information. For both complexes, the optimized average U-O and U-C_{ispo} distances are within 0.04 Å and 0.02 Å, respectively, of those measured in the solid state. This good agreement indicates that the optimized structures are reliable, especially with regard to the U-C_{ispo} distance. According to NLMO (natural localized molecular orbital) analyses (Figure 2 and Table S1), [**1**]$^-$ and [**2**]$^-$ display very similar characteristics for the U-C_{ipso} interactions, which are represented by two-center two-electron σ(U-C_{ispo}) bonds ranging from 22 to 20% uranium character and Wiberg bond orders of 0.67 and 0.60, respectively. The U 5f contributions in these 2c-2e orbitals range from 28% in [**1**]$^-$ to 42% in [**2**]$^-$, whereas the 6d contributions are larger, ranging from 59% in [**1**]$^-$ to 46% in [**2**]$^-$. Not surprisingly, the covalent character of the U-O(THF) interaction in [**2**]$^-$ is much lower, with minor σ and π contributions via donation bonding and a Wiberg bond order of 0.39. For comparison, the uranyl alkyl complex, $[Li(DME)_{1.5}]_2[UO_2(CH_2SiMe_3)_4]$ (**D**), features similar %U character in its U-C bonds (22%), but greater 5f character and lower 6d character (53% 5f vs. 34% 6d).[23]

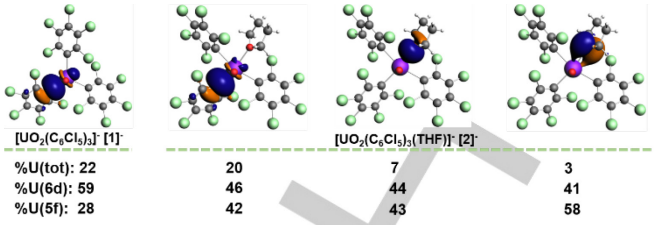


Figure 2. Representative U-L bonding NLMOs in [**1**]$^-$ and [**2**]$^-$. Weight-% metal character and 6d vs. 5f contribution at the metal averaged over equivalent NLMOs. (Isosurface values ±0.03 a.u. Color code for atoms: U purple, O red, Cl seafoam green, C dark gray.)

The ^{13}C NMR chemical shifts for both complexes were calculated without and with effects from SO coupling,[46,47] using a PBE-based hybrid with 40% (and 25%, see SI) exact exchange. This type of calculation has previously provided accurate ^{13}C NMR shifts in actinide compounds.[23,48–50] The averaged calculated C_{ipso} chemical shift for [**1**]$^-$ is 242 ppm, in good agreement with the measured value (237 ppm) given that the calculations necessarily use approximations. SO coupling is responsible for a 62 ppm downfield contribution in this shift, due to the involvement of the 5f (and 6d) subshells in the U-C_{ipso} bonds. For [**2**]$^-$, the calculated chemical shift of the C_{ipso} environment *trans* to THF is 246 ppm, including 68 ppm due to SO effects, whereas the calculated average chemical shift of the C_{ipso} environments *cis* to THF is 261 ppm. Per the bonding breakdown in Figure 2, there is a cancellation of opposite trends due to the added U-O(THF) interaction in [**2**]$^-$: The overall uranium weight in σ(U-C_{ispo}) is slightly lower for the *trans* C_{ipso} environment, but the 5f percentage is higher. The latter is likely responsible for the larger SO shift observed for this environment vs. the SO shift observed for [**1**]$^-$. For comparison, the SO contribution to the ^{13}C chemical shift in **D** was calculated to be much larger (177 ppm),[23] which can be rationalized by the larger 5f contribution to its U-C bonds vs. those found for [**1**]$^-$ and [**2**]$^-$. Significantly, this comparison nicely showcases the exquisite sensitivity of ^{13}C chemical shifts to the 5f participation in An-C bonding.[23,48,51,52]

We also characterized [Li][**1**] and [Li][**2**], along with their ^{18}O-labelled analogues, [Li][**1-^{18}O**] and [Li][**2-^{18}O**], by IR and Raman spectroscopies. Unfortunately, the U=O ν_{asym} modes for neither [Li][**1**] nor [Li][**2**] could be identified in their IR spectra, even with the assistance of isotopic labelling, likely because these modes are buried under ligand vibrations. However, the Raman spectrum of [Li][**1**] exhibits a strong absorption at 834 cm^{-1}, which we have assigned to the U=O ν_{sym} mode. This vibration redshifts to 787 cm^{-1} in the Raman spectrum of [Li][**1-^{18}O**]. The magnitude of this shift (48 cm^{-1}) is similar to those observed previously upon ^{18}O labelling,[15] further confirming our assignment. We also attempted to record Raman spectra for [Li][**2**] and [Li][**2-^{18}O**] but were thwarted by sample decomposition. The ν_{sym} value for [Li][**1**] is comparable to those measured for other uranyl organometallics.[53] For example, the U=O ν_{sym} modes for $[UO_2Cl(\kappa^3\text{-}E(Ph_2PNSiMe_3)_2)(THF)]$ are 829 cm^{-1} (E = N) and 825 cm^{-1} (E = CH), respectively,[20,53] suggesting that the three equatorial ligand sets have comparable donor abilities.

In summary, we have prepared and characterized the first structurally-authenticated uranyl-aryl complexes, $[Li(Et_2O)_2(THF)][UO_2(C_6Cl_5)_3]$ ([Li][**1**]) and

$[Li(THF)_4][UO_2(C_6Cl_5)_3(THF)]$ [Li][**2**], and have confirmed their formulations by X-ray crystallography. A combined ^{13}C NMR spectroscopic and DFT computational analysis reveals that the U-C bonds in [Li][**1**] and [Li][**2**] feature appreciable amounts of covalency with high levels of 5f participation. Moreover, complex [Li][**1**] exhibits good thermal stability in arene solvents, which we believe is a function of the poor reducing ability of the $[C_6Cl_5]^-$ ligand, coupled with the *o*-chloro substitution. The surprisingly good thermal stability suggests that perhalogenated aryl ligands could be broadly useful for the generation of stable actinide aryl complexes, a class of materials that offers many insights into actinide electronic structure and provides excellent benchmarking opportunity for high level quantum chemical calculations.[52,54]

Acknowledgements

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Keywords: uranyl organometallic • actinides • density functional theory • covalency • chemical shift

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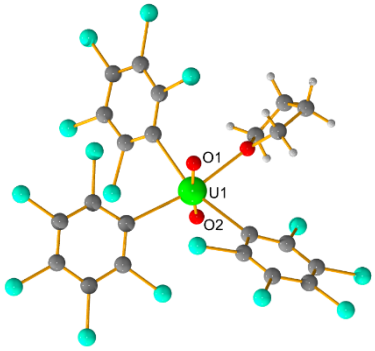

The first structurally characterized uranyl aryl complexes, $[Li(Et_2O)_2(THF)][UO_2(C_6Cl_5)_3]$ and $[Li(THF)_4][UO_2(C_6Cl_5)_3(THF)]$, exhibit appreciable covalency in their U-C bonds, as assayed by a combined ^{13}C NMR spectroscopic and DFT computational analysis.