Low-Valent Uranium (1)

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Coordination and Redox Isomerization in the Reduction of a Uranium(III) Monoarene Complex**

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Abstract: *Synthetic studies on the redox chemistry of trivalent uranium monoarene complexes were undertaken with a complex derived from the chelating tris(aryloxide)arene ligand* $(^{\mathrm{Ad,Me}}\mathrm{ArO})_3\mathrm{mes}^{3-}$. *Cyclic voltammetry of* $[\{(^{\mathrm{Ad,Me}}\mathrm{ArO})_3\mathrm{mes}\}\mathrm{U}^{\mathrm{III}}]$ *(**1**) revealed a nearly reversible and chemically accessible reduction at −2.495 V vs.* $\mathrm{Fc/Fc^+}$*—the first electrochemical evidence for a formally divalent uranium complex. Chemical reduction of **1** indicates that reduction induces coordination and redox isomerization to form a uranium(IV) hydride, and addition of a crown ether results in hydride insertion into the coordinated arene to afford uranium(IV) complexes. This stoichiometric reaction sequence provides structural insight into the mechanism of arene functionalization at diuranium inverted sandwich complexes.*

Transition-metal arene complexes are intermediates in a variety of stoichiometric and catalytic transformations.[1] Recently, diuranium inverted arene complexes have been shown to stoichiometrically borylate arene C−H bonds.[2] While several uranium(III) monoarene complexes have been prepared,[3] the systematic exploration of their redox chemistry has not been pursued (unlike the related diuranium inverted arene complexes),[4] principally because of the lability of the arene ligand. From an electronic structure perspective, these uranium monoarene complexes and the related diuranium inverted arene sandwich complexes are unique due to the involvement of δ bonding between the uranium f orbitals and the arene LUMO.[4c]

We recently reported the synthesis, electronic structure, and $\mathrm{CO_2}$ reductive disproportionation reactivity of a chelating tris(aryloxide) arene uranium complex.[5] Chelating complexes of this type enforce arene δ bonding and potentially provide an opportunity to stabilize lower formal oxidation states. Herein, we report the room temperature reduction and subsequent H-migration processes of the monoarene complex $[\{(^{\mathrm{Ad,Me}}\mathrm{ArO})_3\mathrm{mes}\}\mathrm{U}]$ (**1**; Figure 1). These H-migration events provide a stepwise model for intermediates proposed in the stoichiometric, and potentially catalytic, arene C−H bond borylation chemistry observed for diuranium inverted arene complexes.

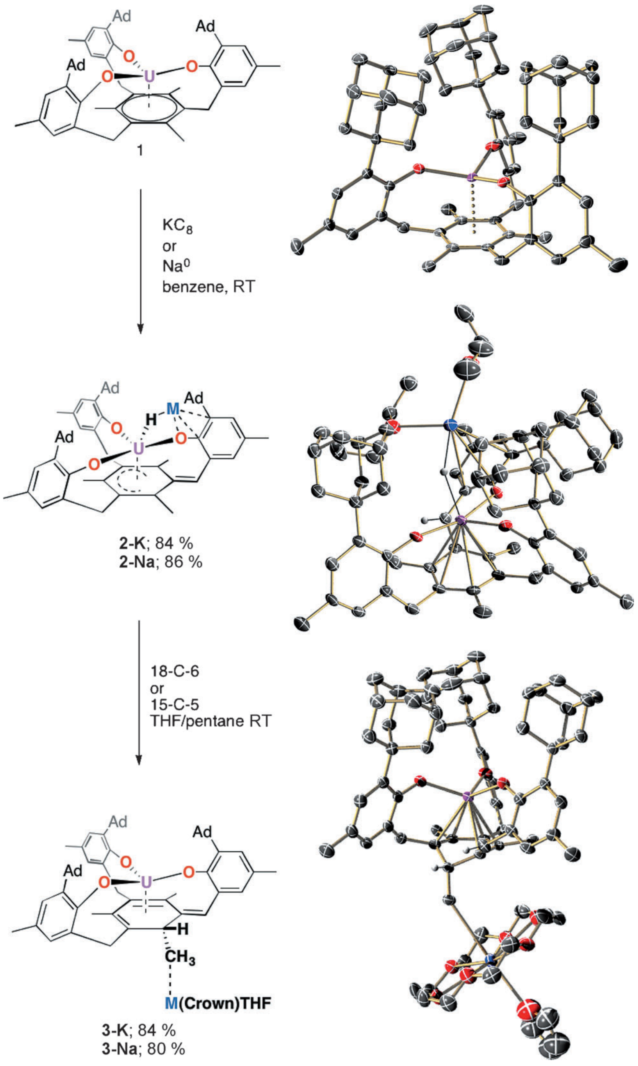

Figure 1. Synthetic conditions for **2-M** and **3-M** with ORTEP representations of **1**, **2-K**, and **3-K**.[15] In the ORTEP representation of **2-K**, the inner-sphere solvents of crystallization (2 diethyl ether molecules) are depicted, but are not present in the isolated powder, which is employed for all other characterization methods. Thermal ellipsoids are shown at 50 % probability.

A chelating tris(aryloxide) arene ligand $[(^{\mathrm{Ad,Me}}\mathrm{ArOH})_3\mathrm{mes}]$ was prepared, which incorporates bulky

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adamantyl groups at the *ortho* positions and methyl groups at the *para* positions of the aryloxide arms to sterically protect the uranium center and increase crystallinity (see the Supporting Information for synthetic details). The complexation of $(^{Ad,Me}ArOH)_3mes$ with uranium(III) is achieved by protonolysis of $[U(N(SiMe_3)_2)_3]$ to give **1** as a deep purple powder in 46 % yield (Figure 1). The molecular structure of **1** (in crystals of $\mathbf{1}\cdot C_7H_8\cdot 2.0\,C_4H_8O$) reveals an idealized C_3-symmetric molecule. The uranium ion lies 0.475(2) Å below the plane defined by the aryloxide oxygen atoms and is centrally located with the O-U-O angles spanning 113.91(9) to 117.51(9)° (sum (∡O-U-O = 346°)). The U−O bond lengths average to 2.168(2) Å. The U−C_{arene} bond lengths are 2.749(3) Å (avg.; U-centroid 2.35 Å), and the C_{arene}−C_{arene} bond lengths are 1.42 Å (avg.). These metric parameters are similar to those of the previously reported *tert*-butyl derivative $[\{(^{tBu,tBu}ArO)_3mes\}U]$.[5a] It should be noted that the average C_{arene}−C_{arene} bond length is within error of that of the free ligand, which suggests that there is little to no reduction of the bound arene ligand (however, this bond metric is not particularly indicative of reduction). Most remarkable is that the average U−C_{arene} bond length is significantly shorter than in the non-chelated $[(\eta^6\text{-}C_6Me_6)U(BH_4)_3]$ (2.93(2) Å).[3f] Additionally, the solid-state magnetic behavior for **1** is similar to that of the previously reported arene complex $[\{(^{tBu,tBu}ArO)_3mes\}U]$.[5a] For **1**, at 300 K, the effective magnetic moment, μ_{eff}, is 1.75 B.M. and decreases to 1.00 B.M. at 5 K (see Figure S16 in the Supporting Information).

Electrochemical investigation of **1** by cyclic voltammetry revealed a near-reversible, chemically accessible one-electron reduction at −2.495 V vs. Fc/Fc$^+$ (at 50 mV s^{-1}; see Figure 2 and the Supporting Information). This chemically accessible reduction suggested that the isolation of a formally divalent uranium arene complex might be possible. However, room temperature reduction of **1** by alkali metal reductants demonstrated subsequent intramolecular chemistry. Treating **1** with KC_8 or Na^0 mirror in benzene gives the uranium(IV) hydride complexes **2-K** and **2-Na** in 84 and 86 % yield, respectively (Figure 1). Loss of the threefold symmetry is clear from the complicated, paramagnetically shifted ^{1}H NMR spectra of **2-K** and **2-Na** compared to that of **1**.

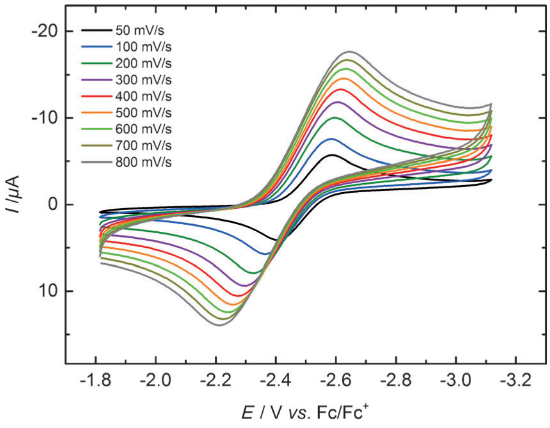


Figure 2. Scan-rate dependence of the reduction of **1**.

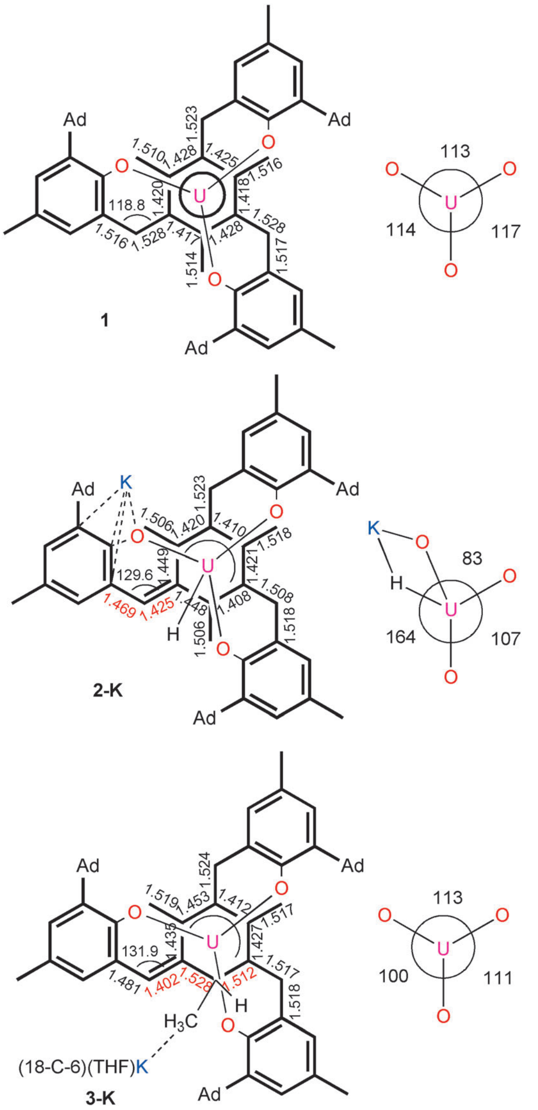


Figure 3. Selected bond lengths and angles for complexes **1**, **2-K**, and **3-K**. O-U-O angles (°) for the complexes depicted on right.

The molecular structure of **2-K**, as determined by XRD on crystals of $\mathbf{2\text{-}K}\cdot 2.0\,C_4H_{10}O$ (Figure 1 and Figure 3), reveals a C_1-symmetric molecule in which the aryloxide arms have undergone a distortion to a T-shaped arrangement about the uranium ion (∡O-U-O, 107.59(13)°, 83.19(13)°, and 164.26(13)°; sum = 355°), with the uranium ion lying just below the plane defined by the aryloxide oxygen atoms (0.199(2) Å). This geometry accommodates a potassium ion bound η^4 to one of the aryloxide arms. The binding of the potassium to the aryloxide results in a longer U−O bond length of (2.232(3) Å vs. 2.144(4) Å and 2.181(3) Å). Additionally, the T-shaped arrangement of the aryloxides affords a seemingly open coordination site at the uranium ion. Close inspection of the Fourier difference map reveals a potential hydride in the expected position between the uranium and potassium ions. While determining the location of hydrides in the coordination sphere of heavy metals by XRD can be difficult, the observed electron density is consistent with a hydride and the observed U−H bond length of 2.050 Å (K−H bond, 2.5219 Å) is consistent with that of bridging U-H-U bonds (2.134(9) Å) which have been measured by neutron diffraction studies.[6]

Furthermore, analysis of the uranium arene bonding and aryloxide benzylic arms in **2-K** implies that H migration from a benzylic ligand arm to the uranium ion to form a hydride has occurred, thus, filling the "open" coordination site of the uranium ion. The U−C_{arene} bond lengths vary from 2.562(5) to 2.907(5) Å, with the shortest adjacent to the benzylic arm of the potassium bound aryloxide. The C−C bonds of the benzylic position are contracted to 1.425(7) and 1.469(7) Å in comparison to 1.529(5) and 1.517(5) Å in **1**. This dramatic contraction in the C−C bonds implies the formation of a pseudo-double bond and hydrogen-atom transfer to the uranium ion (Figure 3). The formation of a uranium(IV) oxidation state in **2-K** and **2-Na** is further confirmed by SQUID measurements.[7] The complex **2-K** has an effective magnetic moment of 2.21 μ_B at 300 K (2.32 μ_B for **2-Na**), which decreases to 0.85 μ_B at 5 K (0.64 μ_B for **2-Na**; see the Supporting Information).

While the hydride resonance cannot be definitively assigned in the ^{1}H NMR spectra,[8] its presence is unambiguously confirmed by reactivity studies. A classic chemical test for the presence of a transition-metal hydrides is its reactivity with CCl_4.[9] The hydrides, **2-K** and **2-Na**, react with CCl_4 to give $CHCl_3$ (as determined by ^{1}H NMR spectroscopy; $\delta =$ 6.15 ppm in C_6D_6) and an insoluble precipitate. More telling is the addition of an appropriate crown ether (18-C-6 for **2-K** and 15-C-5 for **2-Na**), which leads to hydride insertion into the coordinated arene ring, thus forming the complexes **3-K** and **3-Na** in 84 and 80 % yield, respectively, as brown powders (Figure 1).

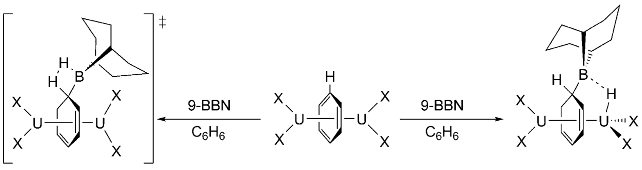
This isomerization and intramolecular, net arene functionalization, is readily seen in the molecular structure of **3-K** in crystals of **3-K**$\cdot 1.5\,C_4H_{10}O \cdot 0.5\,C_4H_8O$ (Figure 1 and Figure 3). In contrast to **2-K**, the uranium ion lies significantly below the plane defined by the aryloxide oxygen atoms (0.769(2) Å) and towards the arene base. The aryloxide arms are arrayed pseudo-trigonally with ∡O-U-O angles of 100.48(9)°, 111.41(9)°, and 113.34(9)° (Sum ∡O-U-O = 325°). The coordination sphere of the C_1 complex is capped by an η^5-pentadienyl moiety with the conjugated C−C bond lengths of the fragment spanning 1.412(5) to 1.453(4) Å. The U−C_{arene} bond lengths are shorter than those in **1** and similar to those in **2-K** (2.546(3) to 2.677(3) Å)). As in **2-K**, one of the benzylic arms is contracted and olefinic in character with C−C bond lengths of 1.402(4) and 1.481(5) Å. Most notably, the sixth "arene" carbon atom lies significantly out of U−C bonding distance (U⋯C; 3.21 Å) and, most importantly, has a tetrahedral geometry. The C−C bond lengths to the remaining portion of the conjugated ligand fragment clearly indicate single-bond character (1.512(4) and 1.528(4) Å), and, in turn, the insertion of the uranium hydride into the arene ring with the formation of a C−H bond. The description of the coordination sphere is completed by noting that the potassium ion and crown ether lie below the arene ring with a close contact between the potassium ion and the methyl group below the hydride insertion site (K⋯C; 3.27 Å).

The complex, paramagnetically shifted ^{1}H NMR spectra of **3-K** and **3-Na** in [D$_8$]THF, are consistent with C_1 symmetry in solution at room temperature, thus suggesting that the solid-state structure is maintained in solution. Similar to **2-K** and **2-Na**, SQUID data imply a formal uranium(IV) oxidation state for both complexes. The complex **3-K** has an effective magnetic moment of 2.22 μ_B at 300 K (2.19 μ_B for **3-Na**), which falls to 0.65 μ_B at 5 K (0.71 μ_B for **3-Na**; see the Supporting Information).

The UV/vis/NIR spectra of **1** and its reduction products **2-M** and **3-M** were also examined (see Figures S8 and S9 in the Supporting Information). The spectrum of **1** is quite similar to that of the previously reported complex $[((^{tBu,tBu}ArO)_3mes)U]$ (as also evidenced by the SQUID and ^{1}H NMR data),[5a] and presents low to mid intensity bands from $\lambda = 450$–900 nm, and can be assigned to Laporte-allowed f to d transitions and, possibly, charge transfer from occupied δ-type U orbitals to the arene's empty π* orbital. The spectra of **2-M** and **3-M** present features similar to those reported for uranium(IV) arene complexes with charge-transfer bands extending through the visible region with weak f–f transitions apparent from $\lambda = 1000$ to 2000 nm.

The near-reversible electrochemical reduction of trivalent **1** is the first electrochemical evidence for a molecular, formally divalent uranium complex.[10] Marks and Burns et al. have previously demonstrated that $[\{Cp^*_2UCl\}_3]$ and $Na[Cp^*_2UCl_2]$ (Cp* = pentamethylcyclopentadienyl anion) can serve as synthetic equivalents of the divalent uranium complex $[Cp^*_2U]$, either by disproportionation in the presence of an oxidant, such as diphenylacetylene, or with Na/Hg and azides or azenes.[11] Evans and co-workers have also shown that $[Cp^*_3U]$ can serve as synthetic equivalent of the divalent uranium through sterically induced reduction.[4f] Yet, Finke and co-workers demonstrated electrochemically that only the $U^{IV/III}$ couple is accessible and reversible and that the $U^{III/II}$ couple is not observed in these Cp*-based systems.[12] The body of elegant work from the group of Evans on divalent lanthanides[13] and, most recently, a crystallographically characterized, formal divalent uranium species,[13d] demonstrates that unusually low formal oxidation state complexes of uranium are synthetically accessible.

The H-migration chemistry observed in the isolation of **2-M** and **3-M** provide a stepwise model for the mechanism of arene C−H borylation proposed by Arnold and Maron.[2] Their DFT calculations suggest that initial uranium(IV) hydride formation (i.e. **2-M**) may be a low-lying intermediate in the reaction with borane [Eq. (1), right: 9-BBN = 9-borabicyclo(3.3.1)nonane]. Product formation in their system may advance by concerted electrophilic aromatic substitution mechanism through a concerted transition state between the bound arene and free borane [Eq. (1), left]. In



the case of the addition of crown ether to **2-M**, the arene functionalization proceeds by hydride insertion to give **3-M**. This hydride insertion chemistry is also reminiscent of arene and cycloheptatetraenyl hydride insertion chemistry described for the transition metals.[14] The scope and utility of this reaction is under further consideration.

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[15] CCDC 977706 (**1**), 977707 (**2-K**), and 977708 (**3-K**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.