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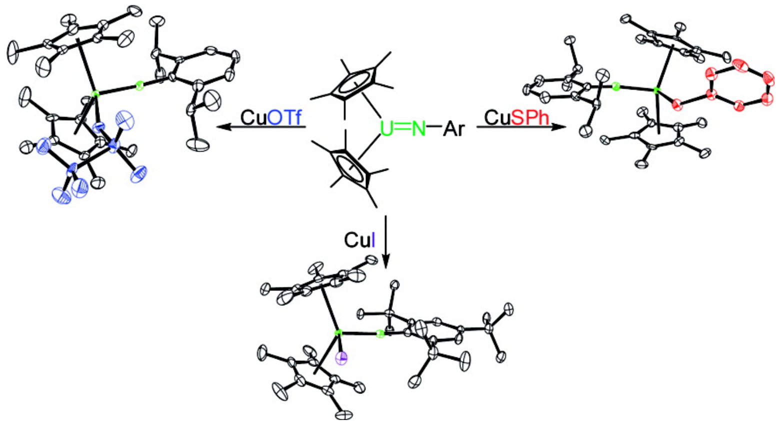

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Facile Access to Pentavalent Uranium Organometallics: One-Electron Oxidation of Uranium(IV) Imido Complexes with Copper(I) Salts

Christopher R. Graves, Brian L. Scott, David E. Morris,* and Jaqueline L. Kiplinger*

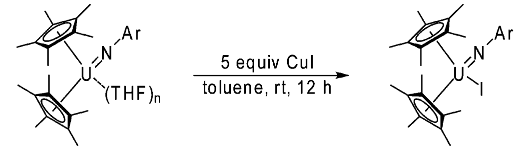
Los Alamos National Laboratory, Los Alamos, New Mexico 87545

Received July 3, 2007; E-mail: kiplinger@lanl.gov

As a direct consequence of their unique and complex properties, organoactinide complexes have found widespread application in a variety of interesting and novel chemical processes.[1,2] While examples of U(IV) and U(VI) organometallics are prevalent in the literature, the corresponding U(V) systems are scarce with little accompanying characterization data.[2,3] Because the roles that the 5f-orbitals play in metal structure, bonding, and reactivity are of the most intriguing concepts in actinide chemistry, and the influence of oxidation state on covalency is a key question, a rational synthetic entry to stable U(V) species for systematic studies of the actinide $5f^1$ electronic configuration is of great interest.

Our recent explorations into electrochemical trends of uranium organometallic complexes[4] revealed a surprisingly accessible reversible one-electron metal-based U(V)/U(IV) redox couple for $(C_5Me_5)_2U({=}N\text{-}2,4,6\text{-}{}^tBu_3{-}C_6H_2)$[4] (**1**) ($E_{1/2} = -0.73$ V vs $[(C_5H_5)_2Fe]^{+/0}$), demonstrating that the electrochemically generated U(V) species of **1** is stable on the voltammetric time scale. Analogous chemical behavior is observed for the sterically less-congested $(C_5Me_5)_2U({=}N\text{-}2,6\text{-}{}^iPr_2{-}C_6H_3)(THF)$ (**2**) ($E_{1/2} = -0.86$ V vs $[(C_5H_5)_2Fe]^{+/0}$). These voltammetric assignments suggest that isolable U(V)−imido organometallic complexes are viable provided a suitable chemical oxidant can be identified.

Surprisingly, copper(I) salts are ideal oxidants for this transformation. Reaction of **1** or **2** with excess copper(I) iodide in toluene affords the corresponding U(V) complexes $(C_5Me_5)_2U({=}N\text{-}2,4,6\text{-}{}^tBu_3{-}C_6H_2)(I)$ (**3**) and $(C_5Me_5)_2U({=}N\text{-}2,6\text{-}{}^iPr_2{-}C_6H_3)(I)$ (**4**), respectively, as dark brown powders in good isolated yield (eq 1). Although silver salts have been successfully utilized as chemical oxidants, the use of Cu(I) salts as oxidizing agents is extremely limited,[6] and to the best of our knowledge, these are the first examples demonstrating the oxidation *and* functionalization of organometallic species using Cu(I) salts.



(1)

1: Ar = 2,4,6-^{t}Bu$_3$-C$_6$H$_2$, n = 0
2: Ar = 2,6-^{i}Pr$_2$-C$_6$H$_3$, n = 1

3: Ar = 2,4,6-^{t}Bu$_3$-C$_6$H$_2$ 78% Yield
4: Ar = 2,6-^{i}Pr$_2$-C$_6$H$_3$ 81% Yield

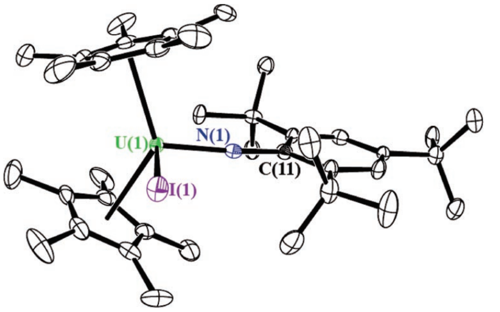
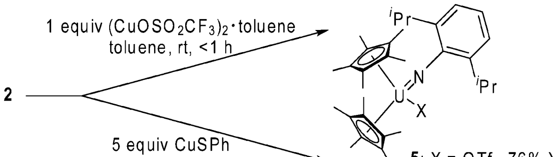


Figure 1. Molecular structure of complex **3** with thermal ellipsoids at the 50% probability level. Selected bond distances (Å) and angles (°): U(1)−I(1) 3.0116(6), U(1)−N(1) 1.975(6), N(1)−C(11) 1.418(8), U(1)−C$_5$Me$_{5(cent)}$ 2.528, N(1)−U(1)−I(1) 97.20(16), C(11)−N(1)−U(1) 169.7(5), C$_5$Me$_{5(cent)}$−U(1)−C$_5$Me$_{5(cent)}$ 130.67.

The ^{1}H NMR spectra of **3** and **4** exhibit a broad signal at ∼6 ppm ($\Delta\nu_{1/2} = 93$ and 125 Hz, respectively) corresponding to the C$_5$Me$_5$ ligand protons. This broadness indicates a hindered rotation about the U═N$_{imido}$ bond as is further evidenced by inequivalency of the *ortho* ^{t}Bu and ^{i}Pr groups in **3** and **4**, respectively, which is not observed in the U(IV) imido starting materials.[5] X-ray diffraction studies confirmed the identity of complexes **3** and **4**[7] as U(V)−imido−iodides. Both feature a typical bent metallocene framework with the imido and iodide ligands contained within the metallocene wedge. Figure 1 presents the molecular structure of complex **3**, which exhibits a nearly linear U(1)−N(1)−C(11) angle (169.7(5)°) and a U(1)−N(1) bond distance of 1.975(6) Å. These metrical parameters compare well with those reported for other U^{IV}/U^{V}/U^{VI} uranium imido complexes.[8] At 3.0116(6) Å, the U(1)−I(1) bond distance falls within the range of other reported U−I bonds.[9]

This Cu(I)-based oxidation protocol appears to be quite general. As shown in eq 2, reaction of **2** with either CuOTf or CuSPh gives the corresponding U(V) triflate (**5**) and phenylthiolate (**6**) complexes, respectively, in good isolated yield. While rapid oxidation of **2** to **5** proceeds at ambient temperature, formation of complex **6** requires elevated temperature. The ^{1}H NMR of both **5** and **6** are analogous to that of **4**, with a broad C$_5$Me$_5$ resonance and inequivalent ^{i}Pr substituents. Additionally, the solid-state structures of both **5**[7] and **6** (Figure 2) reveal nearly identical structures as that observed for **4**, representing rare examples of uranium(V) triflate and thiolate complexes, respectively.[10]



(2)

5: X = OTf, 76% Yield
6: X = SPh, 90% Yield

Like their U(IV) precursors (**1** and **2**), both U(V) imido complexes **3** and **4** exhibit reversible metal-based voltammetric behavior (Figure 3). Specifically, both possess a reduction wave attributed to a U(V)/U(IV) couple ($E_{1/2} = -1.25$ V (**3**) and -1.37 V (**4**) vs $[(C_5H_5)_2Fe]^{+/0}$). Notably, this U(V)/U(IV) couple is shifted to more negative potential by ∼0.5 V relative to the same couple observed in the U(IV) precursors. These U(V) systems also exhibit a reversible U(VI)/U(V) oxidation wave ($E_{1/2} = 0.04$ V (**3**) and 0.11 V (**4**)) that has not been accessible in the U(IV) organometallic complexes investigated to date.[4] Similar electrochemical behavior was observed for both **5** and **6**. This new process to yield a U(VI) species demonstrates the stabilization of the high-valent metal center

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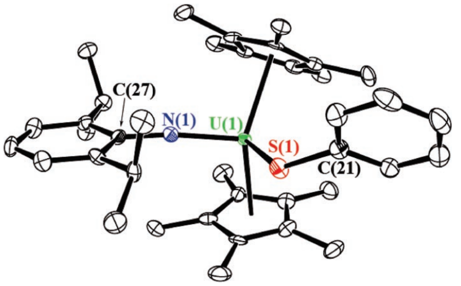

Figure 2. Molecular structure of complex **6** with thermal ellipsoids at the 50% probability level. Selected bond distances (Å) and angles (°): U(1)−S(1) 2.7230(13), U(1)−N(1) 1.976(4), N(1)−C(27) 1.398(6), S(1)−C(21) 1.775(5), U(1)−$C_5Me_{5(cent)}$ 2.457(4), 2.466(4), N(1)−U(1)−S(1) 103.35(12), C(27)−N(1)−U(1) 171.6(3), U(1)−S(1)−C(21) 131.08(17), $C_5Me_{5(cent)}$−U(1)−$C_5Me_{5(cent)}$ 136.2(2).

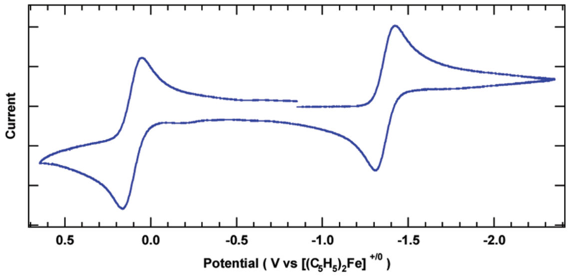

Figure 3. Cyclic voltammogram for $(C_5Me_5)_2U({=}N\text{-}2,6\text{-}{}^iPr_2{-}C_6H_3)(I)$ **4** at a Pt electrode in 0.1 M $[Bu_4N][B(C_6F_5)_4]$/THF at a scan rate of 200 mV/s.

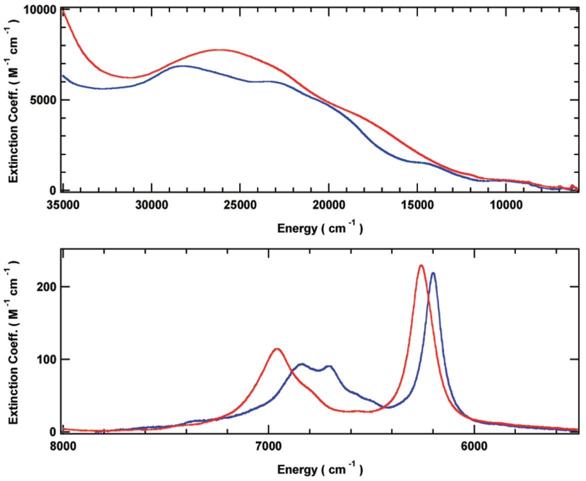

Figure 4. Room temperature electronic absorption spectral data for complexes **3** (red line) and **4** (blue line) in toluene-d_8 solution.

as a result of the metal−imide linkage and the added electron density at the uranium center from the ancillary anionic ligand (e.g., iodide).

These stable U(V) systems provide an opportunity to interrogate the electronic structure of $5f^1$ actinide complexes. The UV−visible region of these spectra (Figure 4, top) is dominated by broad, relatively intense bands ascribed principally to $\pi_{U=N}$-to-nonbonding metal (5f) orbital transitions similar to those seen in early transition-metal imido complexes.[11] Additional narrow, relatively weak bands in the near-IR region (Figure 4, bottom) arise from intraconfiguration ($f-f$) transitions associated with the $5f^1$ valence electronic structure. These bands are comparable in energy and structure to those reported for U(V) halides in much higher symmetry environments.[12] They are assigned to vibronic components of the $\Gamma_7 \rightarrow \Gamma_{7'}$ electronic transition, where the ground and excited states derive from crystal-field splitting of the ground ($^2F_{5/2}$) and excited ($^2F_{7/2}$) spin−orbit manifolds. The relatively minor shifts in these near-IR bands for **3** versus **4** reflect minor differences in the crystal-field perturbation for the two imide ligands. Notably, the energetic proximity of these bands for **3** and **4** versus those for the octahedral halide systems suggests that the spin−orbit coupling is comparable (~2000 cm^{-1}) in all these systems.[12]

In conclusion, we have discovered a general and versatile Cu(I)-based oxidation procedure that enables facile access to pentavalent organouranium complexes. Work focused on elucidating the electronic structure and bonding of these $5f^1$ derivatives, in addition to extending this chemistry to other copper reagents and uranium oxidation states, is currently underway in our laboratory.

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Supporting Information Available: Full experimental and characterization details, and crystallographic data (PDF, CIF) for **3**−**6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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