

Tetravalent and Pentavalent Uranium Acetylide Complexes Prepared by Oxidative Functionalization with $\text{CuC}\equiv\text{CPh}$

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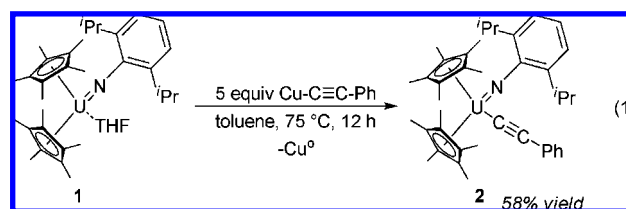
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Summary: Oxidation of $(\text{C}_5\text{Me}_5)_2\text{U}(\text{NPh}_2)(\text{THF})$ and $(\text{C}_5\text{Me}_5)_2\text{U}(=\text{N}-2,6\text{-}^i\text{Pr}_2\text{-C}_6\text{H}_3)(\text{THF})$ with $\text{CuC}\equiv\text{CPh}$ yields the corresponding U^{IV} and U^{V} acetylide complexes $(\text{C}_5\text{Me}_5)_2\text{U}(\text{NPh}_2)(\text{C}\equiv\text{CPh})$ and $(\text{C}_5\text{Me}_5)_2\text{U}(=\text{N}-2,6\text{-}^i\text{Pr}_2\text{-C}_6\text{H}_3)(\text{C}\equiv\text{CPh})$, respectively. The complexes were characterized using a combination of ^1H NMR, X-ray crystallography, UV–visible–near-IR spectroscopy, and cyclic voltammetry.

Despite the key role that the metal alkynyl functionality plays in various homogeneous catalytic processes promoted by organoactinide complexes,¹ only a few examples of actinide complexes exhibiting a terminal acetylide ($\text{AnC}\equiv\text{CR}$) unit have been isolated and structurally characterized.^{2,3} This absence is further underscored when contrasted with the vast number of known transition-metal acetylide complexes.⁴ We recently demonstrated that copper(I) salts are ideal reagents for the preparation of functionalized U^{V} imido complexes from U^{IV} imido precursors.⁵ Given the success of this reaction manifold, we envisioned that organometallic copper acetylide reagents could also be employed in a similar fashion to generate uranium–carbon bonds. Herein, we report a simple procedure for the synthesis of stable tetravalent and pentavalent uranium terminal acetylide complexes using copper(I) phenylacetylide ($\text{CuC}\equiv\text{CPh}$).

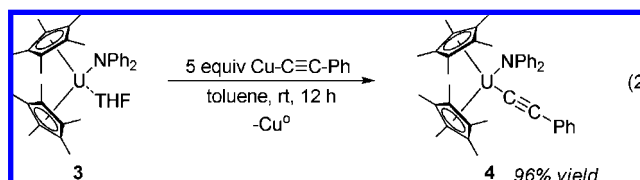
As depicted in eq 1, reaction of $(\text{C}_5\text{Me}_5)_2\text{U}(=\text{N}-2,6\text{-}^i\text{Pr}_2\text{-C}_6\text{H}_3)(\text{THF})$ (**1**) and $\text{CuC}\equiv\text{CPh}$ at 75 °C for 12 h produced the U^{V} acetylide complex $(\text{C}_5\text{Me}_5)_2\text{U}(=\text{N}-2,6\text{-}^i\text{Pr}_2\text{-C}_6\text{H}_3)(\text{C}\equiv\text{CPh})$ (**2**) as a dark brown solid in good isolated yield. Although single

crystals of **2** suitable for X-ray diffraction were not obtained, ^1H NMR, elemental analysis, mass spectrometry, cyclic voltammetry, and UV–visible–near-IR absorption spectroscopy data are consistent with the formulation of **2** as $(\text{C}_5\text{Me}_5)_2\text{U}(=\text{N}-2,6\text{-}^i\text{Pr}_2\text{-C}_6\text{H}_3)(\text{C}\equiv\text{CPh})$. To the best of our knowledge, complex **2** represents the first example of a pentavalent uranium complex with an anionic carbon ligand other than a carbocyclic (C_5R_5 , C_7H_7 , C_8H_8) ligand.⁶



The ^1H NMR spectrum of **2** has diagnostic features comparable to those recorded for the U^{V} imido halides $(\text{C}_5\text{Me}_5)_2\text{U}(=\text{N}-2,6\text{-}^i\text{Pr}_2\text{-C}_6\text{H}_3)(\text{X})$ ($\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}$):^{5b} a broad signal ($\Delta\nu_{1/2} = 80$ Hz) corresponding to the C_5Me_5 ligand protons and inequivalent ^iPr groups. At δ 4.11 ppm, the C_5Me_5 signal for **2** intersects the respective C_5Me_5 resonances for the halide complexes,⁷ indicating that the acetylide ligand is commensurate in donating ability with the fluoride ligand.^{5b} This observation is in accord with electrochemical findings discussed below.

The generality of this Cu-based oxidative functionalization extends beyond the U^{IV} imido system, as demonstrated by the synthesis of the U^{IV} acetylide $(\text{C}_5\text{Me}_5)_2\text{U}(\text{NPh}_2)(\text{C}\equiv\text{CPh})$ (**4**) from the U^{III} amide complex $(\text{C}_5\text{Me}_5)_2\text{U}(\text{NPh}_2)(\text{THF})$ (**3**) (eq 2). This is the first application of any Cu(I)-oxidation protocol to the $\text{U}^{\text{IV}}/\text{U}^{\text{III}}$ redox couple. While elevated temperatures were needed for the synthesis of **2** from **1**, the analogous oxidation of **3** to **4** proceeded smoothly at ambient temperature under otherwise identical reaction conditions in excellent yield.



Single crystals of complex **4** suitable for X-ray diffraction were obtained from the slow evaporation of a concentrated pentane solution at ambient temperature. As shown in Figure 1, **4** features a bent-metallocene framework with the amide and acetylide ligands contained within the metallocene wedge. At 2.409(4) Å, the $\text{U}-\text{C}_{\text{acetylide}}$ bond distance observed in **4** falls within the range of bond distances observed for the three other structurally characterized U^{IV} acetylide complexes. For example, the $(\text{C}_5\text{H}_5)_3\text{U}(\text{C}\equiv\text{CR})$ system has $\text{U}-\text{C}_{\text{acetylide}}$ bond lengths of

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(1) Terminal acetylides have been proposed to be key intermediates in various catalytic processes utilizing actinide organometallic complexes, such as hydrosilylation, alkyne dimerization/oligomerization, and hydroamination. For a detailed account, see: Burns, C. J.; Eisen, M. S. *Homogeneous and Heterogeneous Catalytic Processes Promoted by Organoactinides*. In *The Chemistry of the Actinide and Transactinide Elements*, 3rd ed.; Morss, L. R., Edelstein, N. M., Fuger, J., Eds.; Springer: Dordrecht, The Netherlands, 2006; pp 2911–3012, and references therein.

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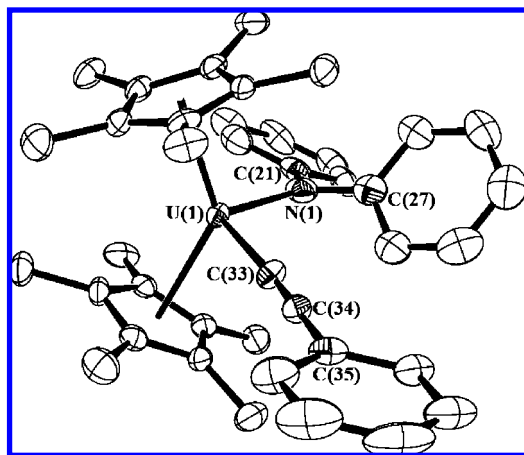


Figure 1. Molecular structure of **4** with thermal ellipsoids projected at the 50% probability level. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg): U(1)–N(1), 2.298(4); U(1)–C(33), 2.409(4); C(33)–C(34), 1.197(6); N(1)–U(1)–C(33), 112.38(15); U(1)–C(33)–C(34), 176.9(4).

2.33–2.36 Å ($R = H$)^{2b} and 2.33(2) Å ($R = Ph$),^{2a} while the U–C_{acetylide} bond distance in the strained uranium metallacycle U[N(CH₂CH₂NSiMe₂Bu)₃](C≡C-4-Me-C₆H₄) is 2.468(7) Å.^{2c} At 176.9(4)° and 1.197(6) Å, the U–C≡C angle and C≡C bond distance in **4** are consistent with the parameters reported for the (C₅H₅)₃U(C≡CR) systems^{2a,b} and analogous transition-metal complexes.⁴

The IR spectra of **2** and **4** were obtained, marking the first report of C≡C stretches for an actinide acetylide system. Both complexes display similar spectra in the high-energy region with bands at 2056 cm^{−1} (for **2**) and 2062 cm^{−1} (for **4**)⁸ that can be assigned to the C≡C stretch by analogy to transition-metal acetylide complexes.⁴

Cyclic voltammetric data for **2** and **4** (Figure 2) are consistent with data reported previously for structurally related pentavalent⁵ and tetravalent^{9,10} uranium metallocene complexes, but the comparison here vividly illustrates the impact of the different ligand sets on the redox energetics for these two oxidation states. The much greater electron-donating ability of the imide ligand in **2** stabilizes the U^{VI} oxidation state, enabling the observation of the U^{VI/IV} redox process while concomitantly destabilizing the U^{V/IV} couple, shifting it to quite negative potential relative to that found in most U^{IV} systems, including the acetylide complex **4**. No further metal-based couples are resolved for the

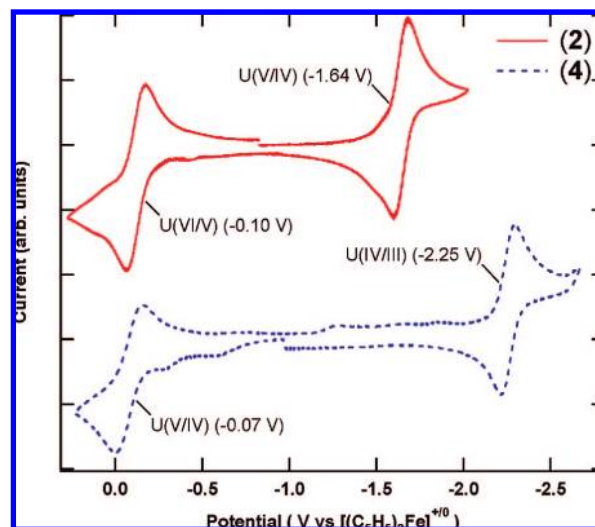


Figure 2. Cyclic voltammograms for **2** and **4** in ~0.1 M [t-Bu₄N][B(1,3-(CF₃)₂-C₆H₃)₄]/THF at a Pt working electrode at 200 mV/s. Half-wave potentials (in parentheses) were determined from peaks in the square-wave voltammograms (not shown).

U^V complex **2**. In contrast, the lesser electron donation from the amide ligand in **4** permits the observation of the U^{IV/III} redox couple, but the U^{VI/V} couple is not accessible.

The separation between the adjacent metal-based redox couples (~1.5 V for **2** and ~2.1 V for **4**) is the same as that found for a wide range of U^V and U^{IV} complexes, respectively.^{5,9,10} On an absolute potential basis, both redox processes for **2** occur at values slightly more negative (~0.1–0.2 V) than those for (C₅Me₅)₂U(=N-2,6-*i*-Pr₂-C₆H₃)(X) (X = Cl, Br, I),^{5b} indicating that the acetylide ligand is a somewhat stronger electron donor than these halides. The potentials for the metal-based couples in **4** are comparable to those found in U^{IV} hydrazonato complexes (C₅Me₅)₂U[η²-(N,N')-CH₃-N=N=CPh₂](X) (X = OSO₂CF₃, Cl) and ~0.25 V more positive than for U^{IV} ketimide complexes (e.g., (C₅Me₅)₂U[–N=C(Ar)₂]₂).^{9,11}

The electronic absorption spectral data for **2** and **4** also provide an informative contrast in electronic structure (Figure 3). In both systems the open-shell 5f electronic configurations give rise to highly characteristic near-infrared intraconfiguration transitions with narrow line widths and relatively low extinction coefficients (ε) commonly associated with f–f transitions. Both complexes also possess broader, more intense spectral bands in the visible and UV region that derive from metal–ligand charge-transfer and ligand-localized excited states. The spectral properties of **2** are very similar to those of other U^V imido complexes, and the assignments are described in detail elsewhere.⁵ The much simpler f–f spectral region (compared to that for **4**) is a consequence of the 5f¹ electronic configuration that gives rise to only two term levels (²F_{5/2} ground-state manifold and ²F_{7/2} excited-state manifold) from spin–orbit coupling. The spectral data for **4** are most like those found for U^{IV} hydrazonato complexes having a 5f² valence electronic configuration.⁹

The most interesting aspect of the spectroscopic data for **2** and **4** is the oscillator strength of the f–f bands. The f–f transitions are parity-forbidden in centrosymmetric systems, and although bent-metallocene complexes of uranium having the generic formulation (C₅Me₅)₂U(L)₂ have much lower sym-

(6) For a selection of pentavalent organouranium complexes with carbocyclic aromatic ligands see: (a) Boisson, C.; Berthet, J.-C.; Lance, M.; Viger, J.; Nierlich, M.; Ephritikhine, M. *J. Chem. Soc., Dalton Trans.* **1996**, 947–953. (b) Gourier, D.; Caurant, D.; Arliguie, T.; Ephritikhine, M. *J. Am. Chem. Soc.* **1998**, *120*, 6084–6092. (c) Boaretto, R.; Roussel, P.; Alcock, N. W.; Kingsley, A. J.; Munslow, I. J.; Sanders, C. J.; Scott, P. J. *Organomet. Chem.* **1999**, *591*, 174–184. (d) Arliguie, T.; Rourmigue, M.; Ephritikhine, M. *Organometallics* **2000**, *19*, 109–111. (e) Burns, C. J.; Eisen, M. S. *Organactinide Chemistry: Synthesis and Characterization*. In *The Chemistry of the Actinide and Transactinide Elements*, 3rd ed.; Morss, L. R., Edelstein, N. M., Fuger, J., Eds.; Springer: Dordrecht, The Netherlands, 2006; pp 2799–2910, and references therein.

(7) The chemical shifts for the C₅Me₅ protons in the ¹H NMR spectrum for (C₅Me₅)₂U(=N-2,6-*i*-Pr₂-C₆H₃)(X) in C₆D₆ are as follows: δ 3.94 ppm (X = F), 4.92 ppm (X = Cl), 5.31 ppm (X = Br), and 5.78 ppm (X = I).

(8) A second stretch was observed in the IR spectrum of complex **4** at 2189 cm^{−1}. Although we cannot rule out this band as an additional C≡C stretching mode, it's usually high energy makes this assignment unlikely.

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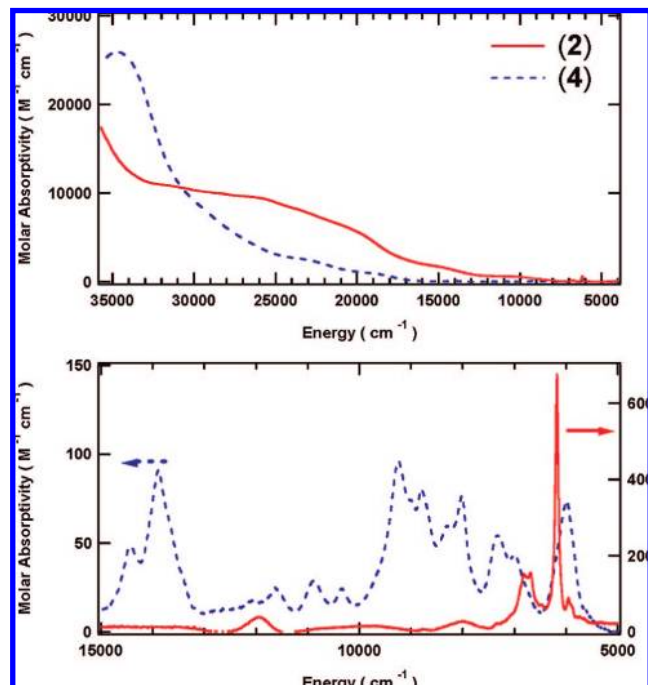


Figure 3. UV–visible (top) and near-IR (bottom) spectral data for **2** and **4** in toluene solution at room temperature. The near-IR spectra have been baseline-corrected to remove the contribution from the higher energy tails of the visible bands.

metries, the f – f transitions are typically still quite weak. For example, in $(C_5Me_5)_2UCl_2$, typical ϵ values for the f – f bands are 20–50 $M^{-1}cm^{-1}$.⁹ In the f – f spectra of **2** and **4** we find substantially greater extinction coefficients that correlate with the intensities and energetic proximity of the visible charge-transfer and ligand-based electronic transitions. This is more

pronounced in the spectrum of **2**, for which the lowest energy bands assigned to metal imide ligand charge-transfer transitions⁵ tail into the near-IR region, and for which the most intense f – f band at $\sim 6100\text{ cm}^{-1}$ has $\epsilon = 650\text{ M}^{-1}\text{ cm}^{-1}$. The enhanced intensities in these f – f bands have been attributed to mixing of these higher lying charge-transfer excited states into the ligand-field states,^{5,9,10} and these new data for **2** and **4** add to the growing body of evidence of the importance of energetic proximities of these higher lying states to enhance the mixing into the f – f states.^{5,9,11}

In conclusion, using $CuC\equiv CPh$ we have shown that Cu-based oxidative functionalization is applicable to both U^{III} and U^{IV} oxidation states through the synthesis of the respective U^{IV} amide and U^V imide acetylide complexes. The isolation of the U^V acetylide complex reported in this work clearly demonstrates that pentavalent uranium can support anionic carbon ligands other than carbocycles and, therefore, may serve as a useful platform for the generation of carbon-based functional groups on uranium.

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Supporting Information Available: Text, tables, figures, and CIF files giving full experimental and characterization details and crystallographic data for **2**–**4**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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