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Tetravalent and Pentavalent Uranium Acetylide Complexes Prepared by Oxidative Functionalization with CuC≡CPh

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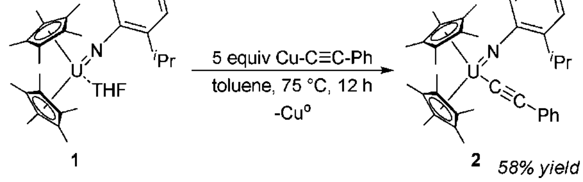
Summary: Oxidation of $(C_5Me_5)_2U(NPh_2)(THF)$ and $(C_5Me_5)_2U({=}N\text{-}2,6\text{-}^iPr_2\text{-}C_6H_3)(THF)$ with CuC≡CPh yields the corresponding U^{IV} and U^{V} acetylide complexes $(C_5Me_5)_2U(NPh_2)(C{\equiv}CPh)$ and $(C_5Me_5)_2U({=}N\text{-}2,6\text{-}^iPr_2\text{-}C_6H_3)(C{\equiv}CPh)$, 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 (AnC≡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 (CuC≡CPh).

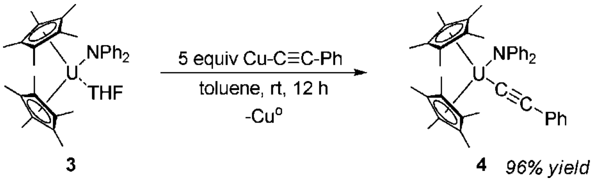
As depicted in eq 1, reaction of $(C_5Me_5)_2U({=}N\text{-}2,6\text{-}^iPr_2\text{-}C_6H_3)(THF)$ (**1**) and CuC≡CPh at 75 °C for 12 h produced the U^{V} acetylide complex $(C_5Me_5)_2U({=}N\text{-}2,6\text{-}^iPr_2\text{-}C_6H_3)(C{\equiv}CPh)$ (**2**) as a dark brown solid in good isolated yield. 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 $(C_5Me_5)_2U({=}N\text{-}2,6\text{-}^iPr_2\text{-}C_6H_3)(C{\equiv}CPh)$. 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]



(1)

The ^1H NMR spectrum of **2** has diagnostic features comparable to those recorded for the U^{V} imido halides $(C_5Me_5)_2U({=}N\text{-}2,6\text{-}^iPr_2\text{-}C_6H_3)(X)$ (X = F, Cl, Br, 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 $(C_5Me_5)_2U(NPh_2)(C{\equiv}CPh)$ (**4**) from the U^{III} amide complex $(C_5Me_5)_2U(NPh_2)(THF)$ (**3**) (eq 2). This is the first application of any Cu(I)-oxidation protocol to the U^{IV}/U^{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.



(2)

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 $U{-}C_{acetylide}$ 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 $(C_5H_5)_3U(C{\equiv}CR)$ system has $U{-}C_{acetylide}$ 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.

[2] (a) Atwood, J. L.; Hains, C. F., Jr.; Tsutsui, M.; Gebala, A. E. *J. Chem. Soc., Chem. Commun.* **1973**, 452–453. (b) Atwood, J. L.; Tsutsui, M.; Ely, N.; Gebala, A. E. *J. Coord. Chem.* **1976**, *5*, 209–215. (c) Boaretto, R.; Roussel, P.; Kingsley, A. J.; Munslow, I. J.; Sanders, C. J.; Alcock, N. W.; Scott, P. *Chem. Commun.* **1999**, 1701–1702.

[3] A handful of lanthanide acetylide complexes have been prepared and structurally characterized: (a) Boncella, J. M.; Tilley, T. D.; Andersen, R. A *J. Chem. Soc., Chem. Commun.* **1984**, 710–712. (b) Evans, W. J.; Ulibarri, T A.; Chamberlain, L. R.; Ziller, J. W., Jr. *Organometallics* **1990**, *9*, 2124–2130. (c) Evans, W. J.; Keyer, R. A.; Ziller, J. W. *Organometallics* **1993**, *12*, 2618–2633. (d) Tazelaar, C. G. J.; Bambirra, S.; van Leusen, D.; Meetsma, A.; Hessen, B.; Teuben, J. H. *Organometallics* **2004**, *23*, 936–939.

[4] Manna, J.; John, K. D.; Hopkins, M. D. *Adv. Organomet. Chem.* **1995**, *38*, 79–154.

[5] (a) Graves, C. R.; Scott, B. L.; Morris, D. E.; Kiplinger, J. L. *J. Am. Chem. Soc.* **2007**, *129*, 11914–11915. (b) Graves, C. R.; Yang, P.; Kozimor, S. A.; Vaughn, A. E.; Clark, D. L.; Conradson, S. D.; Schelter, E. J.; Scott, B. L.; Thompson, J. D.; Hay, P. J.; Morris, D. E.; Kiplinger, J. L. *J. Am. Chem. Soc.* **2008**, *130*, 5272–5285.

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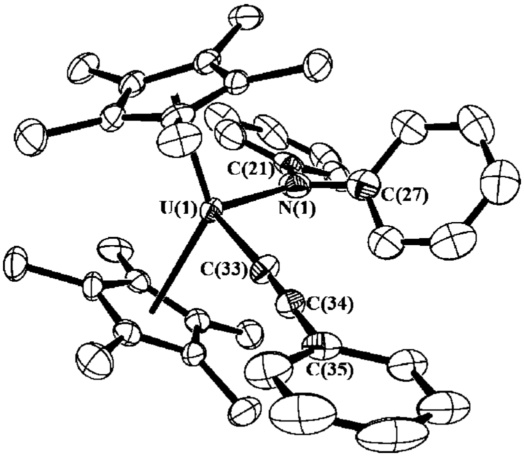

Figure 1. Molecular structure of **4** with thermal ellipsoids projected at the 50% probability level. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg): U(1)−N(1), 2.298(4); U(1)−C(33), 2.409(4); C(33)−C(34), 1.197(6); N(1)−U(1)−C(33), 112.38(15); U(1)−C(33)−C(34), 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(CH$_2$CH$_2$NSiMe$_2{}^t$Bu)$_3$](C≡C-4-Me-C$_6$H$_4$) 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 (C$_5$H$_5$)$_3$U(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 pentavalent[5] 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$^{VI/V}$ 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 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.

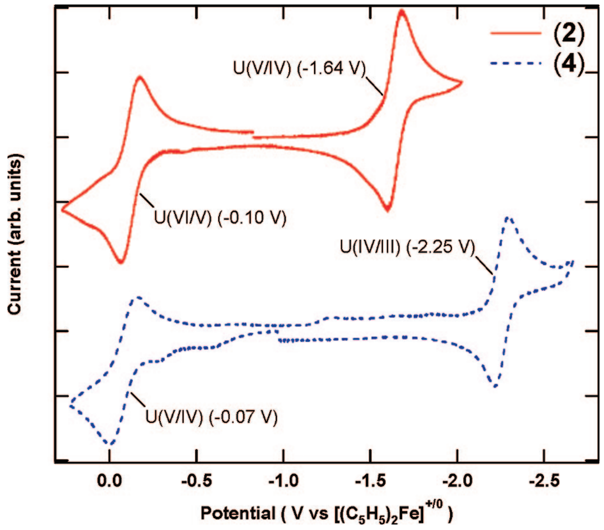

Figure 2. Cyclic voltammograms for **2** and **4** in ∼0.1 M [^{n}Bu$_4$N][B(1,3-(CF$_3$)$_2$-C$_6$H$_3$)$_4$]/THF at a Pt working electrode at 200 mV/s. Half-wave potentials (in parentheses) were determined from peaks in the square-wave voltammograms (not shown).

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 (C$_5$Me$_5$)$_2$U(=N-2,6-^{i}Pr$_2$-C$_6$H$_3$)(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 (C$_5$Me$_5$)$_2$U[η^2-(*N,N'*)-CH$_3$-N-N=CPh$_2$](X) (X = OSO$_2$CF$_3$, Cl) and ∼0.25 V more positive than for U^{IV} ketimide complexes (e.g., (C$_5$Me$_5$)$_2$U[−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 5f^1 electronic configuration that gives rise to only two term levels (^{2}F$_{5/2}$ ground-state manifold and ^{2}F$_{7/2}$ excited-state manifold) from spin−orbit coupling. The spectral data for **4** are most like those found for U^{IV} hydrazonato complexes having a 5f^2 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 (C$_5$Me$_5$)$_2$U(L)$_2$ have much lower sym-

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(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. Organoactinide 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 C$_5$*Me*$_5$ protons in the ^{1}H NMR spectrum for (C$_5$Me$_5$)$_2$U(=N-2,6-^{i}Pr$_2$-C$_6$H$_3$)(X) in C$_6$D$_6$ 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.

(9) Morris, D. E.; Da Re, R. E.; Jantunen, K. C.; Castro-Rodriguez, I.; Kiplinger, J. L. *Organometallics* **2004**, *23*, 5142–5153.

(10) Schelter, E. J.; Yang, P.; Scott, B. L.; Thompson, J. D.; Martin, R. L.; Hay, P. J.; Morris, D. E.; Kiplinger, J. L. *Inorg. Chem.* **2007**, *46*, 7477–7488.

(11) Kiplinger, J. L.; John, K. D.; Morris, D. E.; Scott, B. L.; Burns, C. J. *Organometallics* **2002**, *21*, 4306–4308.

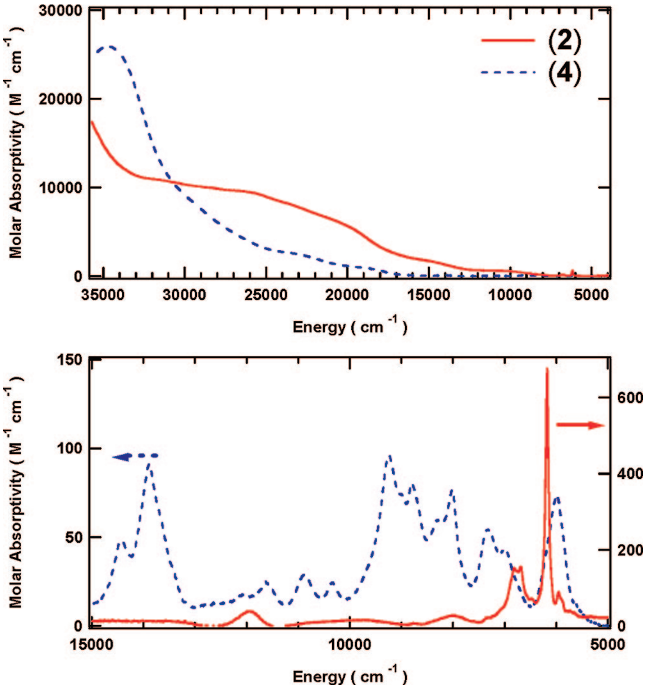

Figure 3. UV−visible (top) and near-IR (bottom) spectral data for **2** and **4** in toluene solution at room temperature. The near-IR spectra have been baseline-corrected to remove the contribution from the higher energy tails of the visible bands.

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 transitions[5] tail into the near-IR region, and for which the most intense f−f band at ~6100 cm^{-1} has $\varepsilon = 650\ M^{-1}\ cm^{-1}$. 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≡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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